



# Hyperspectral imaging applied to the analysis of Goya paintings in the Museum of Zaragoza (Spain)☆



F. Daniel<sup>a</sup>, A. Mounier<sup>a</sup>, J. Pérez-Arantegui<sup>b</sup>, C. Pardos<sup>b</sup>, N. Prieto-Taboada<sup>c</sup>,  
S. Fdez-Ortiz de Vallejuelo<sup>c</sup>, K. Castro<sup>c</sup>

<sup>a</sup> IRAMAT-CRP2A UMR 5060 CNRS-Université Bordeaux Montaigne, 33607 Pessac, France

<sup>b</sup> Instituto Universitario de investigación en Ciencias Ambientales de Aragón (IUCA) and Dep. Química Analítica, Universidad de Zaragoza, 50009 Zaragoza, Spain

<sup>c</sup> Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), 48940 Leioa, Spain

## ARTICLE INFO

### Article history:

Received 20 July 2015

Received in revised form 20 November 2015

Accepted 25 November 2015

Available online 3 December 2015

### Keywords:

Hyperspectral imaging

Raman

EDXRF

In-situ

Non-invasive

Pigments

## ABSTRACT

In recent years, research carried out mostly on paintings has proved that imaging spectroscopy techniques can be used effectively for material identification and mapping on works of art. Regarding the analysis of paintings, the hyperspectral imaging provides the associated reflectance spectrum for every point of the image, which can be compared with those of a reference database. In this work, we evaluated the analytical suitability of two different hyperspectral imaging systems of Goya's paintings kept in the Museum of Zaragoza (Spain). The first one used a "push-broom" system, whereas the second one was a "mirror-scanning" system to study reduced areas. Processing the hyperspectral imaging spectra provided false colour infrared images that showed restored zones of the painting and helped to guide the choice for the pigment analysis of significant zones of the original painting. Their diverse nature, and the presence of complex mixtures, varnishes and organic binders, made the analysis of the pigments difficult, thus, the confirmation by portable Raman Spectroscopy and hand-held X-ray fluorescence was needed. Finally, thanks to the good response of the studied hyperspectral systems, Goya's paintings were mapped and therefore the main pigments used were identified by imaging reflection spectroscopy. In this sense, the availability of a relatively quick procedure would allow a larger number of Goya's paintings in the museum to be surveyed, increasing the possibility of obtaining significant results and providing a chance for extensive comparisons, which are relevant from the point of view of art history issues.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Art studies and the conservation of paintings require knowledge of the materials used, such as colourants, binders, and preparatory layers. This information can also provide insight into the artist's working methods. In this sense, in recent years, research carried out mostly on paintings has proved that imaging spectroscopy techniques can be used effectively for material identification and mapping on works of art [1]. Moreover, the recent advances in the spectro-imaging field [2], as well as the demand for non-invasive techniques for the study of cultural heritage materials, offer a favourable environment for the development of these methods.

The term "hyperspectral imaging" was created by Alexander Goetz in 1985 [3]. It can be considered as the combination of digital imaging with reflectance spectroscopy (applied successfully to conservation through the use of UV–Vis–NIR spectrophotometers) and fibre optic reflectance spectroscopy (FORS). Recently, a state of the art survey [2] concerning hyperspectral imaging redrew the history of these

techniques and applications. Spectral imaging systems provide a powerful tool for non-invasive, non-contact identification and characterization of pigments, inks, substrates and treatments of artefacts, allowing completely non-destructive analyses for research and preservation in archaeology [4], canvas paintings [1,5], illuminations [6–8], wall paintings [9], drawings [10], archives [11], manuscripts [12] and for conservation/restoration purposes [13,14].

As regards red–green–blue imagery (RGB), infrared false-colour (IRFC) and ultraviolet (UV) fluorescence imagery, HSI expand not only the range of possible applications: identifying pigments, monitoring colour changes, colour matching, but also the documentation of IR reflectance and induced UV fluorescence. Imagery and reflectance spectra in the IR range allow the identification of pigments, binders and diverse materials [15,16]. The properties of IR imaging were used, for example, to find the preparatory drawing and to identify pigments [10]. The combination of HSI and spectrofluorescence is an important tool for the non invasive study of organic materials [17]. Indeed, since the 1920s, photographic documentation of fluorescence emitted under UV exposure has been an important diagnostic method for studying historical and artistic objects. Since many inorganic and organic substances exhibit a characteristic emitted fluorescence under UV illumination,

☆ Selected papers presented at TECHNART 2015 Conference, Catania (Italy), April 27–30, 2015.

fluorescence spectroscopy, theoretically, can also be applied to differentiate materials such as resins, pigments and organic binders [18].

Furthermore, spectral imaging has the advantage of being a rapid and relatively low-cost solution for the examination of large areas. It is still too little used for the study of easel paintings. This is because some limitations of the method make its application difficult: 1) when the components of a painting (pigment, binders) are altered, 2) if the underlying materials or complex mixtures of pigments cause spectral interference, 3) when specular reflectance occurs due to varnish, 4) when lights are placed at an unsuitable angle, and 5) if the reference spectral library is incomplete [19]. In spite of these difficulties, HSI is an exciting new field for archaeometry and conservation science and the increase in new developments of studies in cultural heritage objects contribute to its improvement. Moreover, in the particular cases mentioned, the use of complementary techniques solves the problems found. In this sense, portable and hand-held Raman spectroscopy has demonstrated its versatility and adaptability, as well as a very promising performance, as can be seen in scientific studies carried out on rock paintings in caves [20,21], mural paintings [22] or valuable collections in museums [23]. Together with this, portable X-ray fluorescence spectroscopy (EDXRF) has become a very valuable technique in the field of cultural heritage [24,25], for example, in the studies of pottery, cave art, bronzes, and wall paintings.

Taking all of these into account, to study the pigments used by Goya on canvas between 1758 and 1790 inside an on-going project, two different portable HSI systems based on reflection spectroscopy were considered. Thus, the aim of this work was to evaluate the analytical suitability of hyperspectral imaging for identifying original pigments, materials added in restorations, and the painter's technical style.

## 2. Materials and methods

### 2.1. Goya paintings

Francisco de Goya y Lucientes (Fuendetodos, Zaragoza, Spain, 1746 – Bordeaux, France, 1828) was an artist continually training and progressing. Consequently, he tried different genres, and he took an interest in the different styles coexisting in the period when he was working in order to create his own style [26,27]. He was also interested in very diverse techniques and formats: mural painting, oil painting with different dimensions, engraving using various techniques, etc. He was a master of oil painting, creating incredible effects of light, and also of the use of coloured backgrounds (often reddish), that he could leave visible or transparent.

The first painting studied, *'Portrait of a young man with hat'*, belongs to the collection of the Royal Academy of Fine Arts of San Luis, Zaragoza. It appears registered in the catalogue of 1828, as *'Portrait of Francisco Bayeu by his own hand'* [28]. Although, the most recent studies on the works by Francisco Bayeu (Zaragoza, 1734 – Madrid, 1795) prefer to consider this painting as a Bayeu self-portrait, painted around 1758 [29,30], the researchers attributed it to Francisco de Goya, because of its fine quality and because both artists were very close. Bayeu was Goya's brother-in-law and also his teacher between 1759 and 1763. The artist's work is a sketch, a preliminary study where the preparation background is still visible, a red layer made with ochre, which is very characteristic of the Aragonese painters at that time, and which is usually present in many of Goya's paintings. It is a very precise drawing; the painter used the *chiaroscuro*, leaving part of the face in the shadow, a very expressive and natural visage. The man wears a hat on a headscarf tied in the Aragonese style.

The second painting studied was *'Portrait of Juan Martin de Goicoechea y Galarza'* [31]. Goya painted this portrait in 1790. He probably drew some sketches from life in Zaragoza and he finished it later in Madrid, where he lived at that time. Juan Martin was a friend of Goya's, an Enlightenment man, trader and businessman. In 1789 he was awarded the Cross of the Royal Order of Charles III, and this was probably the reason why he

asked his friend Goya for the portrait. On a black background, we can see his upper-body image, in three-quarter position, and looking ahead. He wears a brown dress coat where the medal is outlined. The colours of the face and the right hand really stand out, and the textures of the dress-coat velvet and of the lace in the collar and cuff were very well done.

### 2.2. Hyperspectral imaging

The hyperspectral imaging (HSI) was done on the Goya paintings with two different HSI systems. Regarding the analysis of paintings, for every image point the HSI supplies the associated reflectance spectrum, which can be compared with those of a reference database. In a hyperspectral camera, the light reflected from one line segment of the target sample reaches the entrance slit in the spectrograph. This light is dispersed into different wavelengths by the dispersing element in the spectrograph. This dispersed light is captured by the CCD sensor as a two dimensional image; the spatial position and the spectral dimension. Moving the target object or the spectral camera in a direction perpendicular to a measured line, the HSI system can capture the images of different lines on the target area. By synchronizing the movement between camera and target object and the acquisition of the camera, one can capture different lines of the object and, thus, generate the datacube with the second spatial dimension. The acquisition of reflectance spectra requires a scanning system and for this two methods are possible.

The first one (called HSI-system 1 in this paper) is a "push-broom" system where the scanning is obtained by means of a translation rail. The hyperspectral camera is placed on a translation rail, fixed on two



**Fig. 1.** The different HSI systems and below their corresponding Infrared False Colour Image (IRFC) of "Portrait of a young man with hat" (1758) a) HSI System 2, b) HSI system 1.

tripods (Fig. 1). The camera can be placed vertically or horizontally. The system can be used in fixed configuration for an application in the laboratory or in mobile configuration for in-situ studies in museums or mural paintings. The hyperspectral CCD camera (HS-XX-V10E), developed by SPECIM (Finland), has a  $1600 \times 840$  pixel resolution, a spectral resolution of 2.8 nm and a wavelength range between 400 and 1000 nm. The focal length is 23 mm. The rail allowing the horizontal displacement of the camera system is 1.30 m long and is controlled by the IDAQ software. The paintings were illuminated by two halogen lamps at  $45^\circ$ , 60 cm away from the object. For the study of the paintings, the experimental conditions are: working distance of 114 cm, scan speed of 13 mm/s and exposure time (time for which the CCD array is exposed to light) of 25 ms. This “exposure time” is a characteristic of the CCD sensor. It refers to the specified time interval where the stored charge is accumulated within each CCD photodiode. The duration of a scan depends of the size of the artwork. For the Goya paintings the duration of the scan varied from 30 s to 1 min. At the specified working distance, the halogen lighting delivers 1000 lx onto the surface of the painting, so the illumination level was below the 50 lx·h recommended for fragile objects [32]. Decreasing the illumination by doing binning (adjacent pixels to be combined) would lead to a decrease of the resolution. Spectral IDAQ software provides data acquisition, storage and wavelength calibration.

The second system (“whiskbroom”, called HSI-system 2 in this paper) uses “a mirror-scanning” technique more adapted to the study of reduced areas. The camera, lights and software are the same as described above. The hyperspectral imaging VNIR system (SPECIM, Finland) is composed of the V10E imSpector spectrograph (CCD camera, 30 fps,  $1600 \times 1200$  pixels, 400–1000 nm) and the mirror scanner (optimized from 380 to 1700 nm, field of view:  $80 \times 30^\circ$ —depending on the fore objective lens—, and scan speed between 0.01 and  $25^\circ$ /s). The spectral camera has a slit of 30  $\mu$ m (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 scan speed of the mirror scanner was also optimized in order to obtain good resolved images but avoiding long-time exposures to the halogen lamps. Scan angles of  $25^\circ$  and  $45^\circ$  were used, depending on the size of the painting.

With both HSI systems, calibrated diffuse reflectance targets (Spectralon, by Labsphere, USA) were used to calibrate the resulting spectra. The acquisition of the data was relatively fast (1 min). The treatment of the datacube was performed with ENVI 5.1 + IDL software. The treatment of the datacube gives spectral images and/or identification of the pigments by comparison of the reflectance spectra. One of the main problems with pigment identification using spectral reflectance is the lack of databases of reference pigment and paint. We have our own reference pigment database (>150 reference pigments) mostly characteristic of medieval times (but not only) as our spectral library was built principally for the applications of HSI on illuminations [9]. However, we have to point out that most of these pigments were used in Goya's time and we have added modern pigments to our database. In addition, the CNR-IFAC open-access on-line database of reflectance spectra is available, with the 270 nm–1700 nm spectra of various pigments in common binding media found in Western European paintings [33].

### 2.2.1. RGB and IRFC images

Hyperspectral imaging allows us to obtain images in the visible and near infrared (NIR) ranges. The HSI systems can also identify pigments and map their distribution in a painting by processing the reflectance spectra. In multispectral imaging the RGB and IRFC use broadband filters. In Hyperspectral imaging, specific wavelengths are chosen to achieve this. A natural colour image is obtained by taking three visible bands. Both HSI systems generated data which could be treated by selecting three wavelengths to obtain a red–green–blue (RGB) image (R: 670 nm; G: 550 nm; B: 448 nm) from a matrix of reflectance spectra (400 to 1000 nm) associated with each pixel of the image. IRFC is an

arbitrary construction which in the same analytical conditions allows us to compare a painting to reference pigments. There are a variety of ways to combine two or more spectral bands into a pseudo colour image by selecting some of the other bands (IR, UV, etc.) and assigning them to one of the visible light colour bands (red, green, or blue). Therefore, an infrared false-colour (IRFC) image can also be 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 IRFC image typically distinguishes different pigments that seem the same to the naked eye. Since the 1960s, infrared reflectography is a technique that has been used to look through the paint layers. When the longer wavelengths of infrared radiation penetrate the paint layers, the upper layers appear transparent. The degree of penetration depends on the thickness of the paint, the type of paint used and the length of the wave of infrared radiation. The contrast in the absorption of various materials reveals layers of the painting not visible to the naked eye, such as the underdrawings and changes in the paint layers. For example, the comparison of the IRFC image of the reference pigments with those of the painting allows us to hypothesize about the nature of the pigments [34]. Sometimes, more types of imagery, such as UV fluorescence [35,36], can help to remove uncertainties about the interpretation of IRFC images. A better identification of most of the painting components is done by comparison of the reflectance spectra with fibre optics reflectance spectrometry (FORS) databases [33,37] which allows the pigment mapping (distribution of the endmembers on the surface of the painting).

### 2.2.2. Pigment mapping

By a procedure named “classification”, the software compares the reflectance of the reference spectra of the database with those (endmembers) obtained from the painting. There are different ways to get the spatial distribution of the endmembers/pigments. This can be done by algorithms. One of the most common spectral mapping methods is Spectral Angle Mapper (SAM) [38]. This method considers each spectrum as a vector in an n-dimensional scatter plot (or n-D space). The mathematical treatment computes an angle between the reference and the observed spectrum. Smaller angles represent closer matches to the reference spectrum endmember spectra used by SAM can come from our spectral library. The number of pixels displayed as a specific class is a function of the threshold used to generate the classification. Just because a given pixel is classified as a specific pigment does not mean it is actually that pigment. SAM is a similarity measure, not an identifier. That is why point methods are used to confirm the identification of the endmembers mapped. In this paper, the classification of the HSI data spectra was done using the SAM algorithm (angle 0.4) in order to obtain the spatial distribution of the pigments. However, classifications are not always easy. Regarding the identification of pigments, their diverse nature and the presence of complex mixtures, varnish and organic binders makes the analysis of HSI results difficult in most cases. For example, the mixture of pigments modifies the spectral reflectance behaviour [39]. Little modifications of the spectra, due to a pigment alteration or to a mixture with another pigment or a binder, make the classification impossible if some tolerance of the similarity among spectra is not accepted. Obviously, for interpretation, this method requires the previous creation of a reference spectra database of the components (pigments) of paintings. The quality of the hyperspectral data interpretation (images and spectra) is based on the quality of the database.

In any case, despite algorithms, HSI analysis may need confirmation by other analytical methods such as Raman Spectroscopy and X-ray fluorescence (EDXRF).

### 2.3. In-situ chemical analysis by X-ray fluorescence and Raman spectroscopy

In the case of in-situ analysis, elemental measurements of the samples were carried out by hand-held Energy-Dispersive-X-ray Fluorescence (EDXRF) using an Oxford Instruments (UK) XMET 5100. The instrument



has a rhodium X-ray tube as excitation source, which works at a maximum voltage of 45 kV. The size of the X-ray spot in the instrument used is 9 mm<sup>2</sup>. The analyser has a high resolution silicon drift detector (SDD), with the spectral resolution 20 eV and the energy resolution around 150 eV (calculated at the K- $\alpha$  line of Mn at  $-20^{\circ}\text{C}$ ). The semi-quantitative analyses were performed using a method based on fundamental parameters. The acquisition time for each spectrum was 50 s. Unfortunately, the paintings had a background characterized by a high concentration of lead, which distorts the peaks of the other elements present in the collected spectra. This issue made the interpretation of the data difficult as well as the comparison between the spectra. In order to overcome this problem to some extent, the spectra were Compton-scatter-corrected, by using the characteristic primary radiation from the X-ray source as an internal standard.

On the other hand, the molecular characterization was done by Raman spectroscopy by using a hand-held InnoRaman-ultramobile spectrometer (B&WTEK<sub>INC</sub>, USA) provided with a 785 nm excitation laser with a nominal laser power of 225 mW and a CCD detector (Peltier cooled). All the spectra were obtained with a resolution of 3 cm<sup>-1</sup> in a spectral range of 125–2500 cm<sup>-1</sup>. A BWS 5445–532 s ultramobile Raman spectrometer equipped with a 532 nm green laser (with a maximum power of 43 mW) was also used. The spectrometer works in a range between 62 and 3750 cm<sup>-1</sup> and with a spectral resolution of 4.2 cm<sup>-1</sup>. The integration times, and also the spectra accumulations were set to obtain the better signal-to-noise ratio. The microprobes were handled manually directly on the surface of the paintings. In both cases, the laser power was reduced below 50% of the nominal maximum power to avoid photo-decomposition and/or chemical transformation of the analysed compounds. The acquisition of data was effected with BWSpec software (B&WTEK<sub>INC</sub>, USA) and the analysis, treatment and interpretation of the results was realized with Omnic Nicolet software. The interpretation of the Raman results was accomplished by comparison with standard Raman spectra from the e-Visart and e-Visarch databases [40,41] and spectra obtained from on-line databases such as RRUFF [42,43].

### 3. Results and discussion

Hyperspectral images of the paintings were recorded with both systems (HSI-system 1 and HSI-system 2) and they can be compared in Fig. 1, where the left part was recorded with HSI-system 2 and the right part with HSI-system 1. When HSI-system 1 was used (with the translation rail), the image was taken line by line, and the two halogen lamps moved on the translation rail at the same time as the camera, guaranteeing the reproducibility of the lighting throughout all the scan.

#### 3.1. “Portrait of a young man with hat”, Bayeu, 1758

The visual comparison of the selected pigments of the calibrated IRFC image with those of the database spectra allows us to start to understand the diversity of the pigments used in the painting. In the case of the “Portrait of a young man with hat”, the RGB and IRFC images obtained from the hyperspectral datacube showed restored zones, a uniformity of the pigment used, and a very limited palette (Fig. 2). The processing of datacube spectra gave IRFC images that showed restored zones of the painting and allowed us to guide the choice of analysis of significant areas of the original painting. In Fig. 2b, the IRFC image shows the zones of restoration (in red in the picture). This methodological step was very important at the time of performing in-situ analysis by Raman and EDXRF to obtain reliable results and to not misinterpret the collected data. It is a first approach for the observation of restored zones and for distinguishing different pigments but not for an identification of the pigment. This was obtained by the exploitation of the reflectance spectra.

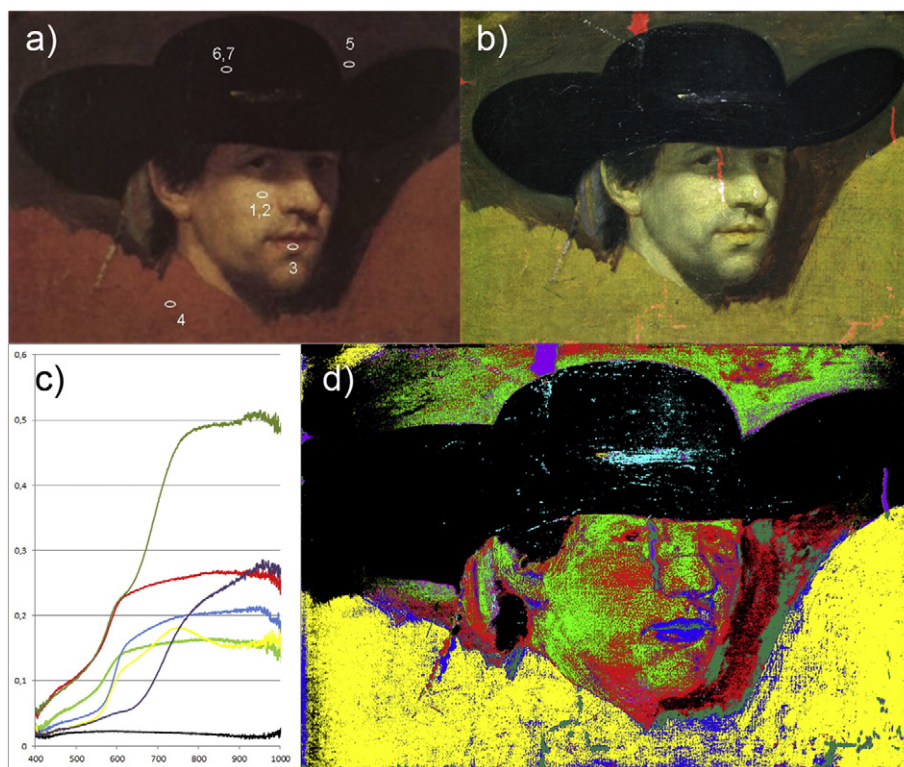
A summary of the resulting reflectance spectra of the pigments is given in Table 1. The painting was well described with the exception

of the black areas. This classification gave a mapping of the different compounds identified (Fig. 2d), a colour code corresponds to each pigment: *blue* (i.e., in the red lips) is vermilion; *black* is in the dark areas where pigments were difficult to identify because the reflectance spectrum has a relatively flat profile and low intensity; the *red* and *green* colour codes correspond to a mixture of vermilion and lead white at different concentrations; the *yellow* zone represents the distribution of red ochre (preparation layer); *violet* and *dark green* (in restored areas) are vermilion mixed with red ochre.

The white areas of the painting were described by the two endmembers found. The most probable white pigments to have been used were lead white and calcite, which cannot be easily distinguished by reflectance spectroscopy. The EDXRF measurement gave a large amount of lead. This element was usually used by Goya as a lead white background to cover his canvas [44]. However, lead has an important absorption coefficient [45] and for this reason, the preparation layer of lead white generated a notable distortion of the EDXRF spectra (Fig. 3a). This fact makes the identification of small amounts of arsenic difficult, for example, because of the overlap of their X-ray lines (As  $K_{\alpha 1} = 10,543$  eV and  $L_{\alpha 1} = 10,551$  eV) [46], being needed for the identification of the secondary line of As ( $K_{\beta 1} = 11,726$  eV). Moreover, it produces different types of artefacts and even the movement of the X-ray lines, caused a decrease in the information obtained from each measurement. Nonetheless, useful analytical information was obtained. In this sense, the EDXRF results indicated lead, sulphur, calcium and iron as major elements, all over the painting. These results could indicate the use of a mixture of compounds in the preparation background, such as calcium carbonate (CaCO<sub>3</sub>) or calcium sulphate (CaSO<sub>4</sub>·2H<sub>2</sub>O), and lead white (2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>).

The two endmembers that mapped to the brown background and the reflectance spectra from sites in this mapped region had the characteristic spectral features of iron oxides. The reflectance spectrum of the preparation-layer endmember had two broad reflectance peaks at 615 nm and 740 nm. According to the reflectance spectra and the pigment mapping (Fig. 2c and d), red ochre was identified in the restored scratches and in the preparatory layer in the lower part of the painting. Taking this into account, regarding the colouration of the painting and although not identified by Raman spectroscopy, the most probable hypothesis was the use of iron oxides for the red background. In fact, the presence of this element in all the analysed points by EDXRF confirmed this hypothesis. Finally, the correlation analysis also showed the intense relation between iron and manganese which reinforced the theory of the use of iron oxides for the painting's reddish background, because both elements are extremely correlated in natural clay pigments such as umber or burnt sienna, two of the standard browns used by artists from the 16th to 19th centuries and consisting mainly of iron and manganese oxides [47].

Bright reds were obtained with vermilion, in particular in the man's lips, whereas flesh was obtained by a mixture of vermilion and lead white in diverse proportions, according to EDXRF analysis (Pb, Hg, S). The chart in Fig. 4 shows the reflectance spectra obtained from different points of the cheek, corresponding to increasing concentrations of lead white. Although the presence of an organic binder would not affect the shape of the spectra, the mixture with lead white gave a low band at 450 nm. Lead white was effectively identified (2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>, main Raman bands at 1049 cm<sup>-1</sup>) in admixture with vermilion (HgS, identified Raman bands at 254 (vs), 343 (s) cm<sup>-1</sup>), mainly found in the face area. Moreover, thanks to the EDXRF analysis, it was possible to observe Hg in the same areas, with the most intense signal in the lips. As a matter of fact, the Raman spectra of the pure vermilion pigment were obtained in this same area, as can be seen in Fig. 3b. Besides, there could be a shift in the inflexion point from 630 to 610 nm probably because of the mixture of pigments (red ochre plus vermilion) (Fig. 4). Additionally, charcoal (amorphous carbon, broad Raman bands at around 1300–1500 cm<sup>-1</sup>) was identified in this artwork. The use of some kind of carbon-based blacks is usually related to this period [48].



**Fig. 2.** a) Visible colour image of “Portrait of a young man with hat” (1758) with zone of Raman analyses; b) false colour near-infrared luminescence image (IRFC) (550, 650, and 900 nm); c) a plot of the reflectance spectra of the end members and d) their associated spatial distributions in the painting. Blue (red lips): vermilion; black: dark zones where the pigments are difficult to identify because the reflectance spectrum has a relatively flat profile and low intensity; red and green colour codes correspond to a mixture of vermilion and lead white at different concentrations; yellow zone represents the distribution of red ochre (preparation layer); violet and dark green (restorations): vermilion + red ochre.

All the restored zones displayed a strong contribution in the infrared range, as we can see in the IRFC image where these areas appeared in red (Fig. 2b) due to a mixture of vermilion and red ochre of the preparation layer. Vermilion was also detected in this area by Raman spectroscopy and it was obvious that some traces of vermilion were present especially in the limits of the portrait and in the preparatory layer zone. However, Raman spectroscopy is a method for point analysis and the presence of some traces of pigments are not necessarily representative of the painted surface. EDXRF would have the advantage of giving more global information about the elemental composition of the different layers because of the higher penetration of the X-rays. However, organic pigments were not recognizable by EDXRF.

In addition, in the non-restored areas, EDXRF showed the unusual presence of Zn and Cd. The presence of Zn could be observed in the reddish areas of the face, maybe because of the use of zinc oxide (ZnO) as a white pigment, or as an impurity of the pigments. Besides, the presence of Cd was detected by EDXRF in non-restored areas, which could indicate

the use of cadmium pigments. This fact would be crucial for dating the painting since these pigments first appeared in 1817 [48], some years after the death of Bayeu (1795) and only eleven years before the demise of Francisco de Goya, and this painting is dated in 1758. Data analysis seemed to indicate that Cd was related to the presence of Pb, that is, Cd was an impurity of the Pb-based pigment. For this reason, and in order to clarify this point, a correlation analysis of the data was carried out. The study revealed, as expected, that Cd, together with another group of elements, was correlated with Pb probably indicating the same origin, such as impurities of the lead white.

### 3.2. “Portrait of Juan Martin de Goicoechea y Galarza”, Goya, 1790

In the portrait of “Juan Martin de Goicoechea”, a painting by Goya, the range of pigments was larger than for the “Portrait of a young man with hat”. The RGB and IRFC images (Fig. 5a and b) did not show visible restorations.

**Table 1**

Palettes of the “Portrait of a young man with hat” and “Don Juan de Goicoechea”, x = colourant identified by the technique (for XRF: indication of key-elements); s. = colourant suggested by the technique; n.i. = colourant not identified by the technique.

Hue	“Young man”	“Don Juan”	HSI reflectance spectra		XRF	Raman
Red	Vermilion + lead white	Vermilion + red lake	x	450 <sup>a</sup> , 610 <sup>b</sup>	x	x
		Red Ochre	x	630 <sup>b</sup>	x	x
	Red ochre	Red Ochre	x	615 <sup>a</sup> , 740 <sup>a</sup>	x	n.i.
White	Lead white	Lead white	s.	— <sup>c</sup>	x	x
	Calcite	Calcite	s.	— <sup>c</sup>	s.	x
Black	Carbon black	Carbon black	n.i.	— <sup>c</sup>	n.i.	x
Blue		Prussian blue	s.	460 <sup>a</sup>	n.i.	x

<sup>a</sup> Apparent absorbance maximum.

<sup>b</sup> Inflection point.

<sup>c</sup> No clear spectral feature detectable.

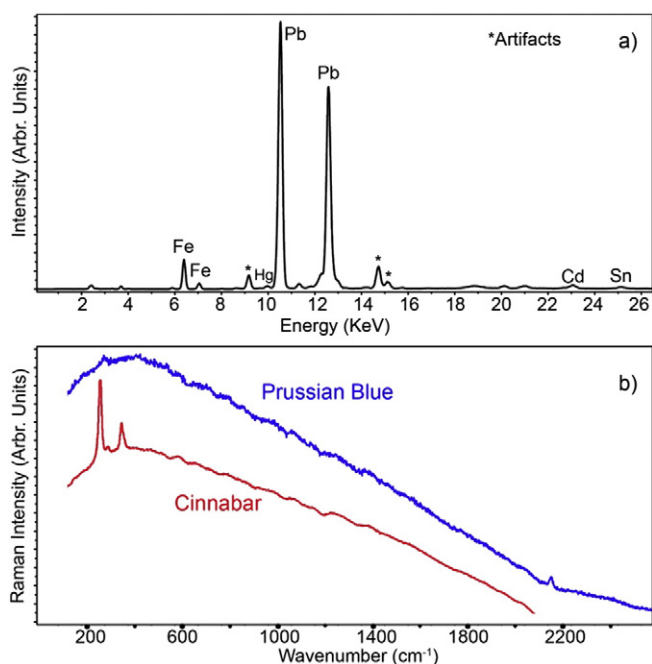


Fig. 3. a) EDXRF spectrum of a black point of the "Portrait of a young man with hat" where the high presence of lead is observed. b) Pure vermilion pigment Raman spectrum obtained from the "Portrait of a young man with hat" painting and the Raman spectrum of the Prussian blue identified in the medal ribbon of the "Juan Martin de Goicoechea" artwork.

The classification of HS datacube spectra gave a mapping of the different identified pigments (Fig. 5c). In Fig. 5d, each colour code corresponds to a pigment: *dark red* to vermilion mixed with red ochre and lead white; *pink* (cheek) to vermilion; *light blue* and *violet* to a mixture of a red lake with vermilion; *dark grey* (ribbon of the medal) and *black* to a non identified pigment; *green* (hair) to calcite.

The HSI mapping showed that the endmember that maps to the mantle and face had a reflectance transition edge at 630 nm. Vermilion (HgS) has a transition edge position around 610 nm [37]. The shift of this transition edge at 630 is probably due to a red lake which has

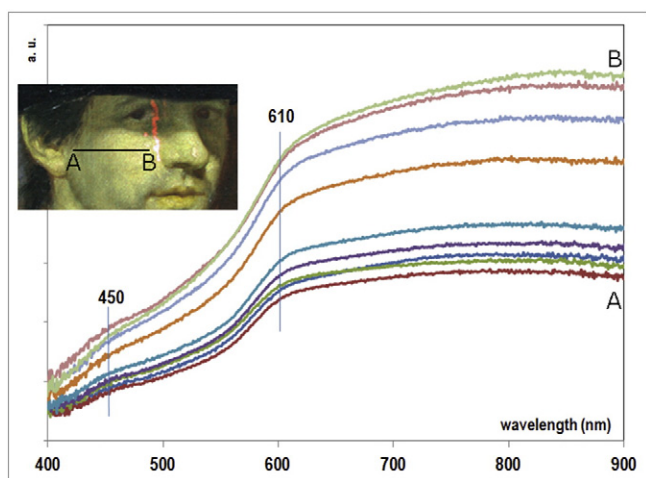


Fig. 4. Reflectance spectra on the cheek of the "Portrait of a young man with hat", 1758. The contribution at 450 nm corresponds to the lead white mixed with the vermilion. From the bottom up the different spectra show low concentrations of lead white in the mixture to high concentrations.

transition edges at higher wavelengths and the classification suggested this. The reflectance spectrum was well described by vermilion mixed with lead white. EDXRF analysis at a site within the mapped area confirmed the presence of mercury, which is consistent with the vermilion assignment, and lead.

The white pigments of the painting were described by the two endmembers that were found. The first one was lead white, consistent with the reflection spectral analysis, mixed with vermilion. The EDXRF measurement found a large amount of lead. The second white pigment (calcite) was localized in the hair of Juan Martin.

Prussian blue ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ) was used for the darker blue of the medal ribbon and detected by Raman bands observed at 268 (m) and 2153 (s)  $\text{cm}^{-1}$  (see Fig. 3b). This pigment, already usual at that time, had indeed been discovered by 1706. Despite these results which agreed with the EDXRF and Raman results, the endmembers and associated map showed that the reflectance spectra from the same zone did not correspond to the usual shape of Prussian blue, since the spectral assignment of this pigment is made based on the low reflectance in the red. The intensity and maximum reflectance varied from 440 to 460 nm, depending of the dilution with lead white pigment [49]. It is possible that the presence of varnish or the mixture with another pigment modified the shape of the Prussian blue reflectance spectra.

Vermilion and lead white were also found by Raman spectroscopy. The first pigment was identified mainly in the lip and cheek areas for the flesh colour, mixed with lead white and, sometimes, with calcium carbonate ( $\text{CaCO}_3$ , main Raman band at 1082  $\text{cm}^{-1}$ ). Lead white was also identified in the white areas of the hair and shirt. Regarding the EDXRF analysis, the presence of Hg in the lips and cheeks corroborated the identification of vermilion by Raman spectroscopy.

In addition, the presence of iron in the red areas of the jacket indicated, probably, the use of iron oxides such as red earth. In the case of the black background, the presence of iron was also notable. However, in this case, a higher presence of copper together with calcium was determined. EDXRF elemental analysis performed on the jacket suggested the presence of iron earths and white pigments (lead white).

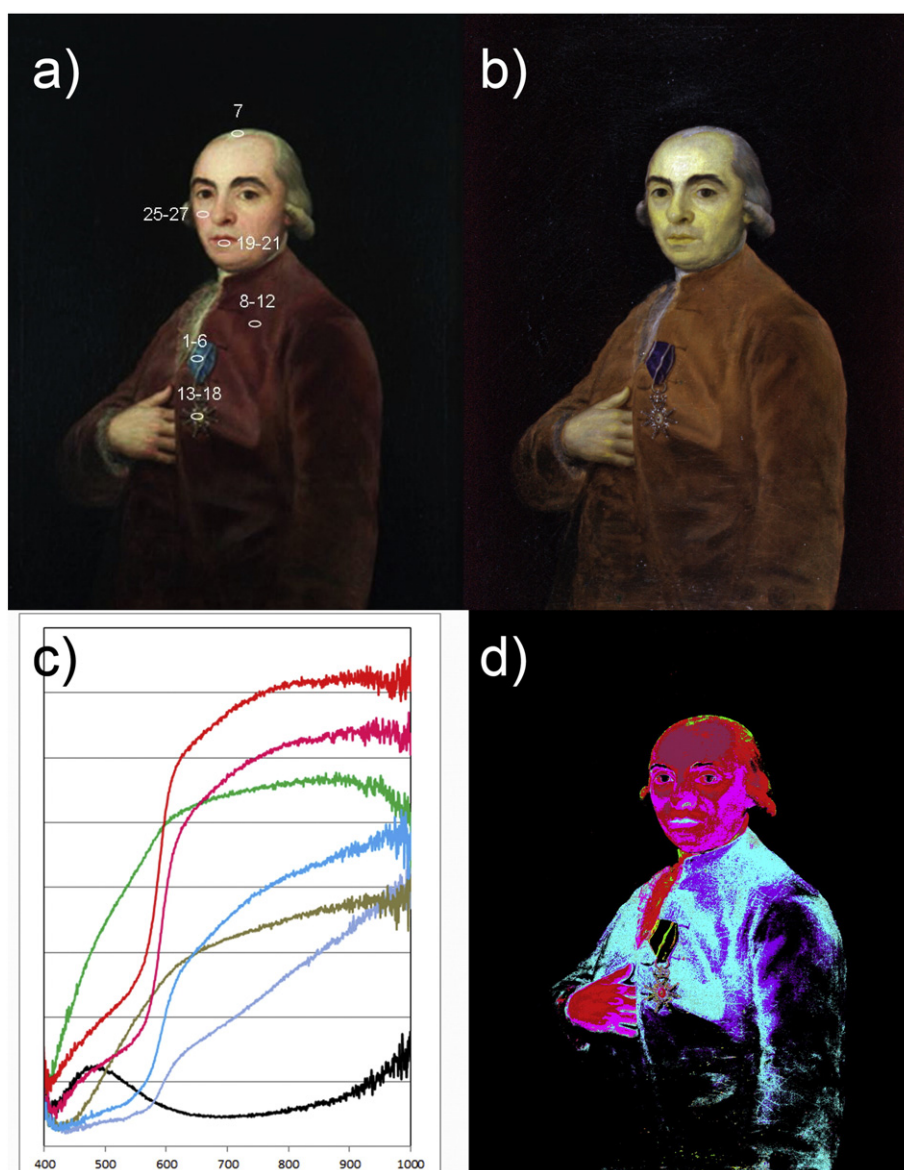
As in the "Portrait of a young man with hat", the face was painted with a mixture of vermilion and lead white, as shown by EDXRF analysis (Pb, Hg, S), in diverse proportions. The hair was painted with calcite. Iron was also detected in the face. Reflectance spectra in the same zones showed the presence of ochre.

In this artwork, as in the previous one, cadmium was identified in all the measured points. Data analysis of the EDXRF results revealed once again the correlation between lead and a group of elements, as in the case of the "Portrait of a young man with hat", in which cadmium was included. This group of elements was similar in both paintings with mainly the presence of Cd, Sr, Zr, Cl and S. Finally, iron and manganese were also correlated in this artwork.

#### 4. Conclusions

All the analysed pigments corresponded to those used at the time of Goya and this has already been established in previous publications [45]. However, the hyperspectral imaging allowed us to determine the non-restored zones and to make hypotheses about the nature of the pigments used by comparing the reflectance spectra with those of our reference database. The two hyperspectral systems gave comparable results, from the "Portrait of a young man with hat" (1758) almost monochrome to the "Portrait of Juan Martin de Goicoechea y Galarza" (1790), where the palette was widened. In both paintings, the painter used a red preparatory layer (red ochre or burnt earths), which proves the widespread use of this technique among the Aragonese painters of that period. Moreover, vermilion more or less lit up or darkened with lead white or carbon based pigments, was also used in both portraits. Besides these more common pigments, on the portrait of Juan Martin de Goicoechea, Prussian blue was identified.





**Fig. 5.** a) Visible colour image (RGB) of “Portrait of Juan Martin de Goicoechea” (1790) with zone of Raman analyses; b) false colour near-infrared luminescence image (IRFC) (550, 650, and 900 nm); c) a plot of the reflectance spectra of the end members and d) their associated spatial distributions in the painting. Dark red: vermilion + red ochre + lead white; pink (cheek): vermilion; light blue and violet: mixture red lake + vermilion; dark grey (ribbon of the medal): non identified; black: non identified; green (hair): calcite.

However, the mixture of pigments and the presence of varnish made some interpretations difficult. Thus, additional methods such as Raman spectrometry and X-ray Fluorescence were necessary to confirm the hypotheses. With hyperspectral imaging there are some uncertainties in the interpretation of the reflectance spectra. Another difficulty occurs when superficial non-homogeneity and compositional complexity of the pictorial material make the analytical identification more complex. Besides, sometimes, the mixture of pigments modifies the shape of the reflectance spectra. It is clear that new algorithms have to be developed for the mapping of complex mixtures of materials.

Concerning the differences between both HSI facilities, the HSI-system 1 give high quality images allowing relevant post treatment (image, mapping) and interpretation of the data. The HSI-system 2 showed some advantages related to mobility (low weight and dimensions) and for scanning small areas, but achieving uniformity of lighting was more difficult because the light system had a fixed position, especially when large areas were studied.

Raman spectroscopy also presents some features that make the interpretation of the spectra difficult, which is the case of fluorescence,

and that is probably due to the presence of varnish and/or protective layers. In addition, EDXRF spectra were totally conditioned by the presence of a high amount of lead.

In conclusion, hyperspectral imaging can be applied to fragile paintings, without damage, for the location and identification of materials. Moreover, this system allows the highlighting of the complexity of the drawing and the lights and the diversity of the pigments used. The analysis gave a global vision of the distribution of pigments and their possible changes, as well as reporting on the state of the object (losses of pictorial material) or chemical changes.

#### Acknowledgements

This study was carried out within the framework of a 2013–14 project financed by the *Communauté de Travail des Pyrénées Grant number 12012223 - Comunidad de Trabajo de los Pirineos*, with the partnership of three regions: Aragon (IUCA-Universidad de Zaragoza), Basque Country (Universidad del País Vasco, CTP2012-P10) and the Aquitaine region (IRAMAT-CRPA, CNRS-University Bordeaux Montaigne). Thanks also

to the Museum of Zaragoza, and especially to Marisa Arguis and Carmen Gallego from the Painting Department. N. Prieto-Taboada is grateful to the University of the Basque Country (UPV/EHU) for her post-doctoral contract.

## References

- [1] J.K. Delaney, J.G. Zeibel, M. Thoury, R. Littleton, K.M. Morales, M. Palmer, E.R. de la Rie, Visible and infrared reflectance imaging spectroscopy of paintings: pigment mapping and improved infrared reflectography, *Proc. SPIE, O3A: Optics for Arts, Architecture, and Archaeology II*, 73912009 03 (7391).
- [2] H. Liang, Advances in multispectral and hyperspectral imaging for archaeology and art conservation, *Appl. Phys. A Mater. Sci. Process.* 106 (2012) 309–323.
- [3] J.S. MacDonald, S.L. Ustin, M.E. Schaepman, The contributions of Dr. Alexander F.H. Goetz to imaging spectrometry, *Remote Sens. Environ.* 113 (2009) S2–S4.
- [4] C. Bassani, R.M. Cavalli, R. Goffredo, A. Palombo, S. Pascucci, S. Pignatti, Specific spectral bands for different land cover contexts to improve the efficiency of remote sensing archaeological prospection: the Arpi case study, *J. Cult. Herit.* 10 (Supplement 1) (2009) e41–e48.
- [5] D. Lau, C. Villis, S. Furman, M. Livett, Multispectral and hyperspectral image analysis of elemental and micro-Raman maps of cross-sections from a 16th century painting, *Anal. Chim. Acta* 610 (2008) 15–24.
- [6] A. Mounier, G. Le Bourdon, C. Schupetit, C. Belin, L. Servant, S. Lazare, Y. Lefrais, F. Daniel, Hyperspectral imaging, spectrofluorimetry, FORS and XRF for the non-invasive study of medieval miniatures materials, *Herit. Sci.* 2 (2014) 1–12.
- [7] A. Mounier, F. Daniel, Hyperspectral imaging for the study of two mediaeval Italian miniatures (XIIIth c.) in the MARCADE Collection, *Stud. Conserv.* 60 (Suppl. 1) (2015) <http://dx.doi.org/10.1179/0039363015Z.S200.000000000225>.
- [8] J.K. Delaney, L.D. Glinsman, M. Facini, M. Thoury, M. Palmer, E.R.d.l. Rie, Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts, *Stud. Conserv.* 59 (2014) 91–101.
- [9] H. Liang, A. Lucian, R. Lange, C.S. Cheung, B. Su, Remote spectral imaging with simultaneous extraction of 3D topography for historical wall paintings, *ISPRS J. Photogramm. Remote Sens.* 95 (2014) 13–22.
- [10] M. Attas, E. Cloutis, C. Collins, D. Goltz, C. Majzels, J.R. Mansfield, H.H. Mantsch, Near-infrared spectroscopic imaging in art conservation: investigation of drawing constituents, *J. Cult. Herit.* 4 (2003) 127–136.
- [11] R. Padoan, M.E. Klein, G. de Bruin, B.J. Aalderink, T.A.G. Steemers, Monitoring aging processes of archival documents by means of quantitative hyperspectral imaging: a part of the hyperspectral project at the Nationaal Archief (National Archives of the Netherlands), *The Book and Paper Group Annual*, 282009 63–72.
- [12] E. Marengo, M. Manfredi, O. Zerbinati, E. Robotti, E. Mazzucco, F. Gosetti, G. Bearman, F. France, P. Shor, Development of a technique based on multi-spectral imaging for monitoring the conservation of cultural heritage objects, *Anal. Chim. Acta* 706 (2011) 229–237.
- [13] V. Papadakis, A. Loukaiti, P. Pouli, A spectral imaging methodology for determining on-line the optimum cleaning level of stonework, *J. Cult. Herit.* 11 (2010) 325–328.
- [14] S. Joo Kim, F. Deng, M.S. Brown, Visual enhancement of old documents with hyperspectral imaging, *Pattern Recogn.* 44 (2011) 1461–1469.
- [15] P. Ricciardi, J.K. Delaney, Combining visible and infrared imaging spectroscopy with site specific, in-situ techniques for material identification and mapping, *Rev. Hist. Arte* 1 (2011) 253–261.
- [16] J.R. Mansfield, M. Attas, C. Majzels, E. Cloutis, C. Collins, H.H. Mantsch, Near infrared spectroscopic reflectance imaging: a new tool in art conservation, *Vib. Spectrosc.* 28 (2002) 59–66.
- [17] M. Romani, F. Colao, R. Fantoni, M. Guiso, M.L. Santarelli, Hyperspectral fluorescence for organic pigment characterization in contemporary artwork, *J. Appl. Laser Spectrosc.* 1 (2014) 29–36.
- [18] A. Mounier, C. Belin, F. Daniel, Spectrofluorimetric study of the ageing of mixtures used in the gildings of mediaeval wall paintings, *Environ. Sci. Pollut. Res.* 18 (2011) 772–782.
- [19] M. Kubik, Chapter 5 hyperspectral imaging: a new technique for the non-invasive study of artworks, in: D. Creagh, D. Bradley (Eds.), *Physical Techniques in the Study of Art, Archaeology and Cultural Heritage*, 1st, 1st edition Elsevier Science, The Netherlands 2007, pp. 199–259.
- [20] A. Hernanz, J.M. Gavira-Vallejo, J.F. Ruiz-López, S. Martín, Á. Maroto-Valiente, R. de Balbín-Behrmann, M. Menéndez, J.J. Alcolea-González, Spectroscopy of Palaeolithic rock paintings from the Tito Bustillo and El Buxu Caves, Asturias, Spain, *J. Raman Spectrosc.* 43 (2012) 1644–1650.
- [21] M. Olivares, K. Castro, M.S. Corchón, D. Gárate, X. Murelaga, A. Sarmiento, N. Etxebarria, Non-invasive portable instrumentation to study Palaeolithic rock paintings: the case of La Peña Cave in San Roman de Candamo (Asturias, Spain), *J. Archeol. Sci.* 40 (2013) 1354–1360.
- [22] M. Maguregui, U. Knuutinen, I. Martínez-Arkarazo, A. Giakoumaki, K. Castro, J.M. Madariaga, Field Raman analysis to diagnose the conservation state of excavated walls and wall paintings in the archaeological site of Pompeii (Italy), *J. Raman Spectrosc.* 43 (2012) 1747–1753.
- [23] P. Colomban, A. Tournié, M.C. Caggiani, C. Paris, Pigments and enamelling/gilding technology of Mamluk mosque lamps and bottle, *J. Raman Spectrosc.* 43 (2012) 1975–1984.
- [24] G. Simsek, F. Casadio, P. Colomban, L. Bellot-Gurlet, K.T. Faber, G. Zelleke, V. Milande, E. Moinet, On-site identification of early BÖTTGER red stoneware made at Meissen using portable XRF: 1, body analysis, *J. Am. Ceram. Soc.* 97 (2014) 2745–2754.
- [25] L. Beck, H. Rousselière, J. Castaing, A. Duran, M. Lebon, B. Moignard, F. Plassard, First use of portable system coupling X-ray diffraction and X-ray fluorescence for in-situ analysis of prehistoric rock art, *Talanta* 129 (2014) 459–464.
- [26] V. Bozal, Goya, Machado Libros D. L., Madrid, 2010.
- [27] N. Glendinning, *Arte, ideología y originalidad en la obra de Goya*, Universidad de Salamanca, Salamanca, 2008.
- [28] F. Torralba Soriano, A. Ansón Navarro, Goya realidad e imagen; Museo de Zaragoza, 3 de octubre - 1 de diciembre, 1996, Electa, Madrid, 1996 1746–1828.
- [29] A. Ansón Navarro, I. Gutiérrez Pastor, J.M. de la Mano, Francisco Bayeu y Sus Discípulos, Cajalón, Zaragoza, 2007.
- [30] A. Ansón Navarro, Los Bayeu, una familia de artistas de la ilustración, Caja Inmaculada, Zaragoza, 2012.
- [31] F. Beltrán Lloris, G.M. Borrás Gualis, La Memoria De Goya (1828–1978), Gobierno de Aragón, Zaragoza, 2008.
- [32] S. Michalski, The Lighting Decision. Fabric of an Exhibition, Preprints of Textile Symposium 97, Canadian Conservation Institute, Ottawa, 1997 97–104.
- [33] Institute of Applied Physics (IFAC), Fiber Optics Reflectance Spectra (FORS) of Pictorial Materials in the 270–1700 nm range, <http://fors.ifac.cnr.it/index.php2011>.
- [34] T. Moon, M.R. Schilling, S. Thirkettle, A note on the use of false-colour infrared photography in conservation, *Stud. Conserv.* 37 (1992) 42–52.
- [35] A. Mounier, S. Lazare, F. Daniel, A new portable LEDpSF device for fragile artworks analyses: applications on medieval pigments, Technart 2015: Non-destructive and microanalytical techniques in art and cultural heritage 2015 06.
- [36] A. Cosentino, Identification of pigments by multispectral imaging; a flowchart method, *Herit. Sci.* 2 (2014) 1–12.
- [37] A. Cosentino, FORS spectral database of historical pigments in different binders, *Environ. Conserv. J.* 2 (2014) 57–68.
- [38] P. Ricciardi, J.K. Delaney, M. Facini, L. Glinsman, Use of imaging spectroscopy and in situ analytical methods for the characterization of the materials and techniques of 15th century illuminated manuscripts, *J. Am. Inst. Conserv.* 52 (1) (2013) 13–29.
- [39] T. Cavaleri, A. Giovagnoli, M. Nervo, Pigments and mixtures identification by visible reflectance spectroscopy, *Proc. Chem.* 8 (2013) 45–54.
- [40] M. Pérez-Alonso, K. Castro, J.M. Madariaga, Vibrational spectroscopic techniques for the analysis of artefacts with historical, artistic and archaeological value, *Curr. Anal. Chem.* 2 (2006) 89–100.
- [41] K. Castro, M. Pérez-Alonso, M.D. Rodríguez-Laso, L.Á. Fernández, J.M. Madariaga, On-line FT-Raman and dispersive Raman spectra database of artists' materials (e-VISART database), *Anal. Bioanal. Chem.* 382 (2005) 248–258.
- [42] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD), *Spectrochim. Acta A* 53 (1997) 2159–2179.
- [43] R.T. Downs, The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals, Anonymous Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan 2006, pp. 003–013.
- [44] R. Bruquetas, T. Antelo, Á. Arteaga, P. Borrego, M. Bueso, M. del Egidio, A. Gabaldón, M. Gómez, C. Martín de Hijas, C. Vega, D. Juanes, Estudio técnico de Fernando VII a caballo de Francisco de Goya, *Bienes Cult.* 8 (2008) 117–132.
- [45] J.H. Hubbell, S.M. Seltzer, Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients 1 keV to 20 MeV for elements Z = 1 to 92 and 48 additional substances of dosimetric interest, The National Institute of Standards and Technology (NIST). NISTIR-56321995.
- [46] M. Gräfe, E. Donner, R.N. Collins, E. Lombi, Speciation of metal(loid)s in environmental samples by X-ray absorption spectroscopy: a critical review, *Anal. Chim. Acta* 822 (2014) 1–22.
- [47] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *The Pigment Compendium: A Dictionary of Historical Pigments*, Butterworth Heinemann, Italy, 2008.
- [48] J.R. Barnett, S. Miller, E. Pearce, Colour and art: a brief history of pigments, *Opt. Laser Technol.* 38 (2006) 445–453.
- [49] J. Kirby, D. Saunders, Fading and colour change of prussian blue: methods of manufacture and the influence of extenders, *National Gallery Technical Bulletin*, 252004 73–99.