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Characterization of Sorolla's gouache pigments by means of spectroscopic techniques

Clodoaldo Roldán [a,*], David Juanes [b], Livio Ferrazza [b], Jorgelina Carballo [a]

[a] Instituto de Ciencia de los Materiales de la Universidad de Valencia (ICMUV), C/Catedrático José Beltrán, 2, 46980 Paterna, Valencia, Spain
[b] CulturArts Generalitat, Subdirección de Conservación, Restauración e Investigación (IVC+R), C/Genaro Lahuerta, 25, 46010 Valencia, Spain

HIGHLIGHTS

- Gouache pigments have been identified by portable EDXRF spectrometry.
- OM and SEM-EDX analyses reveals the structure of the paint layer.
- Sorolla's sketches for the Vision of Spain have been analyzed for the first time.

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ABSTRACT

This paper presents the characterization of the Joaquín Sorolla's gouache sketches for the oil on canvas series “Vision of Spain” commissioned by A. M. Huntington to decorate the library of the Hispanic Society of America in New York. The analyses were focused on the identification of the elemental composition of the gouache pigments by means of portable EDXRF spectrometry in a non-destructive mode. Additionally, SEM-EDX and FTIR analyses of a selected set of micro-samples were carried out to identify completely the pigments, the paint technique and the binding media. The obtained results have confirmed the identification of lead and zinc white, vermillion, earth pigments, ochre, zinc yellow, chrome yellow, ultramarine, Prussian blue, chromium based and copper–arsenic based green pigments, bone black and carbon based black pigments, and the use of gum arabic as binding media in the gouache pigments.

1. Introduction

The preliminary gouache paintings for the series Vision of Spain represent the sketches painted by Joaquín Sorolla to decorate the library of the Hispanic Society of America in New York. Archer Milton Huntington commissioned Sorolla in 1911, and over the next years he travelled throughout Spain producing the preparatory sketches before painting the 14 oil on canvas panels of the Vision of Spain in 1919. These sketches, made during 1912–1914, depict some of the regions of the country showing, as stated in the contract, the rural life, costumes, traditions and landscapes of Spain at the beginning of the 20th century. The Vision of Spain constitutes altogether an ethnographic approximation to the regions of Spain that is chronicled in the preparatory gouache sketches, studies and large format oil on canvas panels (VV., 1998; 2008). The gouache pigments were applied on paper supports of different quality, colour, thickness and textures. The sketches cover a wide spectrum of themes that have been recurrent in his artistic production: landscapes and life scenes of local customs and manners, the popular and religious festivals, the public institutions, etc.

In this creation, Sorolla was working in an extremely experimental manner using the gouaches as a kind of aesthetic laboratory for developing his ideas in form of rapid drawings and brushstrokes to make scenes, persons, animals, objects and landscapes that afterwards cut out and assemble to reconstruct a collage with the desired composition. Our purpose has been to fill the gap of information about the composition of the gouache pigments used by Sorolla in these 32 sketches of the “Vision of Spain” and to provide analytical data that could contribute to their conservation and restoration process. This work offers the opportunity to complement and increase the previous physicochemical studies of the materials and techniques of Joaquín Sorolla's paintings in the early twentieth century (Ferrero et al., 2002; Juanes and Gómez, 2008; Roldán et al., 2011), a period characterized by complex

* Corresponding author.
E-mail address: clodoaldo.roldan@uv.es (C. Roldán).

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paintings techniques with new materials that are present from the 19th century due to the industrial expansion of synthetic pigments.

The identification of gouache pigments was performed by means of portable Energy Dispersive X-Ray Fluorescence spectroscopy (EDXRF) in a non-destructive mode. Afterwards, micro-samples were taken from selected zones of the gouache pigments and analysed them by a combination of Optical Microscopy imaging (OM), Scanning Electron Microscopy with microanalysis (SEM-EDX) and Fourier Transform Infrared spectroscopy (FTIR). Although these techniques have become established analytical tools for the study of great variety of painting materials (Hradril et al., 2007; Roldán et al., 2010; Van der Snickt et al., 2010; Alfeld et al., 2011; Salvadó et al., 2013; Fontana et al., 2014), analyses of gouache pigments are scarce and, in the case of the Sorolla's paintings, are non-existent.

These techniques allowed the characterization of gouache pigments, the layered structure of the paintings and the presence of organic binders. The great advantage of the portable EDXRF spectrometry is its non-invasive character because no contact or sampling is necessary and all the surface of the gouache sketches can be easily analysed. On the other hand, EDXRF analyses can determine points of interest on the paint surface to perform a micro sampling study with other analytical techniques. Certainly, obtaining micro-samples is an essential requirement if it is important to obtain information about the stratigraphy of the paint layers and the artist's technique. This study has given us the opportunity to obtain information of the composition of this kind of pigments used by Joaquín Sorolla at the beginning of the 20th century, in the sketches Vision of Spain, and has provided the opportunity to compare the data obtained by the in-situ non-invasive approach of a complex painting structure with the data from paint cross sections obtained by conventional micro-sampling techniques.

2. Material and methods

The sketches for the Vision of Spain painted by Joaquín Sorolla are collages of gouache paintings (combined occasionally with the use of oil) on low-quality papers. The sketches showed signs of deterioration as surface cracking, flaking, fragmentation and splitting of the painting layer, caused by the thickly applied impasto paint, the tensions of the underlying paper and an excessive use of adhesive when different figures and compositions are superimposed in several layers. Table 1 shows the identification codes used in this study, their references at the Hispanic Society of America (HSA) archives, the subject matter represented in the sketch, the date and dimensions. A set of selected images of the sketches is shown in Fig. 1. In these works, Sorolla uses a technique based on quick and fluent drawings that sometimes blurs with washes and gouaches and offers an extraordinary sense of the composition through the use of the colour: touches of red on grey compositions, miscellaneous of green and blue, intense yellows, variations of brown, pink washes, etc. Some sketches present a subjacent charcoal drawing under the gouache pigments and one

Table 1
Sorolla's sketches for the "Vision of Spain" from the Hispanic Society of America collection: references, titles, dates and number of analysed points in the different coloured areas.

Sketch	HSA reference	Title	Date	Dimensions (cm)	Number of analyzed points										
					Paper	Yellow	Blue	White	Brown	Orange	Black	Red	Green	Violet	***TOTAL***
V-28	A1520	Basque Provinces	ca.1912–13	117.5 × 207.1	1	2	4	3	3	0	4	4	6	0	***27***
V-29	A1524/1	Triptyc: part 1	ca.1912–13	117.5 × 216.0	0	2	6	2	3	2	2	1	7	0	***25***
V-30	A1524/2	Triptyc: part 2	ca.1912–13	117.5 × 216.0	1	2	7	2	4	0	2	3	7	0	***28***
V-31	A1524/3	Triptyc: part 3	ca.1912–13	117.9 × 103.1	1	1	1	0	1	0	1	1	2	0	***8***
V-32	A1526	Navarra	ca.1912–13	135.0 × 198.7	1	2	1	2	2	0	2	2	0	0	***12***
V-33	A1527 recto	Castilla	ca.1912–13	138.8 × 208.0	1	5	2	2	8	0	2	3	4	0	***27***
	A1527 verso	Castilla	ca.1912–13	138.8 × 208.0				2			1				***3***
V-34	A1530	Castilla	ca. 1912–13	137.6 × 200.1	1	3	2	1	5	0	4	2	5	1	***24***
V-35	A1531	Castilla	ca. 1912–13	135.1 × 200	1	3	2	2	2	0	3	0	2	0	***15***
V-36	A1541	Castilla	ca. 1912–13	93.8 × 138.2	1	0	0	1	0	0	4	0	0	0	***6***
V-37	A1536	Bullfight	ca. 1912–13	134.1 × 120.8	2	1	0	1	3	0	2	1	1	0	***11***
V-38	A1538	Prelates	ca. 1912–13	131.3 × 136.4	1	0	0	2	0	0	2	2	0	0	***7***
V-39	A1540	Installation plan	ca. 1912–13	86.1 × 101.2	1	0	0	1	0	0	2	0	0	0	***4***
V-40	A1543/1	Castilla	ca. 1912–13	115.5 × 114.6	2	2	3	2	3	0	2	2	4	1	***21***
V-41	A1543/3	Castilla	ca. 1912–13	115.4 × 122.1	1	2	3	1	2	1	3	3	2	0	***18***
V-42	A1543/2	Castilla	ca. 1912–13	1116 × 121	2	3	4	2	1	0	2	2	0	0	***16***
V-43	A1545	Castilla	ca. 1912–13	101.5 × 130.2	1	3	4	2	2	0	3	1	3	1	***20***
V-44	A1547/1	Castilla	ca. 1912–13	134.7 × 166.0	3	1	2	2	4	0	3	3	5	0	***23***
V-45	A1547/2	Castilla	ca. 1912–13	134.5 × 188.4	1	1	2	2	3	0	3	3	2	0	***17***
V-46	A1548	Basque provinces	ca. 1912–13	135.3 × 190.5	1	0	1	1	4	1	3	1	5	0	***17***
V-47	A1554	Drummers	ca. 1912–13	46.5 × 51.0	1	1	2	4	2	1	3	4	4	0	***22***
V-48	A1555	Asturias (fragment)	ca. 1912–13	43.4 × 44.0	5	1	2	1	0	0	2	1	0	0	***12***
V-49	A1556	Figures	ca. 1912–13	66.4 × 59.6	4	0	1	2	3	0	2	2	7	0	***21***
V-50	A1557	Figures	ca. 1912-13	119.0 × 56.5	3	6	3	7	10	0	11	4	15	0	***59***
V-51	A1558	Figures	ca. 1912-13	114.4 × 96.7	2	6	4	3	5	0	6	8	6	0	***40***
V-52	A1559	Figures	ca. 1912-13	38.5 × 38.4	3	3	4	6	4	1	5	4	5	2	***37***
V-53	A1560	Figures	ca. 1912-13	42.8 × 73.0	2	1	1	2	3	0	5	4	5	1	***24***
V-54	A1561	Figures	ca. 1912-13	53.2 × 87.0	5	0	3	3	3	0	3	3	1	0	***21***
V-55	A1562	Sketches of figures	ca. 1912-13	126.4 × 51.5	1	1	2	2	3	0	5	4	3	0	***21***
V-56	A1564	Man with oxcart	ca. 1912-13	47.7 × 67.2	2	1	1	1	1	0	1	2	2	1	***12***
V-57	A1565	Seated figure	ca. 1912-13	43.8 × 67.0	2	0	3	1	1	0	1	1	3	1	***13***
V-58	A1566	Man with oxcart (fragment)	ca. 1912–14	55.2 × 70.7	2	2	2	1	2	0	2	1	5	0	***17***
V-59	A1568	Men with oxcart	ca. 1912–14	87.0 × 117.8	2	0	3	1	2	0	3	0	1	0	***12***
				Totals	***57***	***55***	***75***	***67***	***89***	***6***	***99***	***72***	***112***	***8***	***640***

Fig. 1. Selected images of the 32 preparatory sketches for the "Vision of Spain" work.

of them (sketch V39: study for the distribution of the murals for the library of the Hispanic Society) was made in charcoal.

The focus of the research was the painting materials, and for studying the elemental composition of the pigments we used two types of analyses: (a) in situ and non-destructive analysis in order to preserve the integrity of paintings; and (b) ex situ analysis of a limited set micro-samples from the gouache sketches in order to complement the limitations of the EDXRF analysis in the complex

Fig. 2. The portable EDXRF spectrometer during analysis of the Sorolla's gouache sketches.

case of the Sorolla painting technique.

Non-destructive analysis of the paintings were made in situ at the building of the Subdirección de Conservación, Restauración e Investigación, CulturArts Generlitat (IVC+R) using a portable EDXRF spectrometer (Fig. 2) made with a miniaturized X-ray tube with silver anode operating in transmission mode and a Peltier cooled Si-PIN detector with a resolution of 170 eV (FWHM @ 5.9 keV). The X-ray tube and detector are orientated in a 45° geometry and the beam impinges perpendicular to the sample. The sample-detector distance was controlled by means of two laser diodes and fixed to 1.5 cm in order to increase the geometric efficiency of the system. Tube and detector were mounted on a mechanical support that allows us XYZ movements to place the system in front of the analysis point and to maintain the same geometry ensuring the reproducibility of the measurements. An aluminium collimator with a diameter of 3 mm was used to define an irradiated spot of about 80 mm^2 on the sample. The excitation parameters of the spectrometer were a fixed voltage of 30 kV, a current of 4 μA and an acquisition time of 180 s. These parameters are appropriate to excite and detect the fluorescence lines of a wide range of elements with an acceptable statistical significance. The resulting EDXRF spectra were evaluated using the PyMCA software package (Solé et al.; 2007) and the fluorescence peak areas were normalized to the total count of the spectra in order to diminish geometrical effects and fluctuations of the tube intensity.

After the preliminary characterization of the elemental composition of the pigments via EDXRF spectroscopy, a selected set of sub-millimetre micro-samples ($<0.5\ mm^2$) were collected to identify and to analyse the structure of the paint layers by optical microscopy (OM) imaging and scanning electron microscopy imaging with microanalysis. These studies were conducted using a NIKON ECLIPSE 80i optical microscope with visible and ultraviolet light sources and a Hitachi S-3400N VP-SEM equipped with a BRUKER XFlash© energy dispersive X-ray spectrometer operating at 20 kV and a working distance of 10 mm. Previously, the micro-samples were prepared on cross-sections and embedded in polyester or epoxy resin for cutting and polishing them perpendicularly to their surface.

Micro-FTIR analyses of the organic binders were obtained with a BRUKER Vertex 70 spectrometer attached to BRUKER microscope Hyperion 2000 operating in transmission mode using a 15× objective, energy range of 4000–400 cm^{-1} and resolution of 4 cm^{-1}. FTIR spectra were recorded using 64 scans on samples placed on a KBr ground pellets of 13 mm in diameter.

3. Results and discussion

A total of 640 EDXRF spectra were obtained from the underlying paper and from white, red, orange, yellow, green, blue, violet, brown and black pigments. Table 2 shows an overview of the distribution of the EDXRF measurement points in the 32 Sorolla's sketches. The number of analysed points of each sketch was function of its dimensions and the colours and hues that it showed. The identification of the inorganic pigments is based on their visual information as the colour and the correlation between the chemical elements identified in the EDXRF spectra and the named "key elements" of a plausible catalogue of pigments compatible with the documentation of the author's palette (Miliani et al., 2007; Van der Snickt et al., 2010; Roldán et al., 2011; McGlinchey, 2012). Pigments composed by light elements or organic pigments such as lakes or carbon based black pigments cannot be directly detected by EDXRF spectrometry, but their presence can be postulated by the absence of certain heavy elements associated with the investigated colour. We have selected uniform brushstrokes that delimit homogeneous colour areas larger than the spot of the X-ray to avoid interferences with other pigments from perimeter areas of the analysis point.

In this work we have combined EDXRF spectrometry with SEM-EDX to obtain a more comprehensive knowledge of the painting materials. SEM-EDX offers spatial, stratigraphic and elemental information as result as the analysis of micro-samples embedded in resin (Pinna et al., 2000). Samples were taken after the EDXRF measurements from painted areas of the sketches with ambiguous identification of the pigments and from areas with superposition of pigment layers to shed light on the layering of paints. FTIR spectroscopy provides information about organic components in paint (Stuart, 2007). The non-destructive EDXRF analysis and the SEM-EDX and FTIR analysis of the micro-samples have led the following results regarding the identification of painting technique, the gouache pigments and the organic binders of the Sorolla's sketches "Vision of Spain".

3.1. Painting technique

Gouache is a paint that contains a pigment, an opacifier (usually an opaque white inert pigment), a binder and a plasticizer. Seeing that the opacifier dilutes the coloured pigment, more pigment must be added to compensate this whiteness, so both opacifier and/or a higher concentration of pigment may be necessary to get opaque paints across a full range of hues. Elements as calcium and barium are frequently detected in the EDXRF analyses. These elements could be related to the use of calcium and barium compounds (chalk, gypsum, barium sulphate, …) as fillers in paints or could be present as extenders in the composition of the pigments (Gettens, Stout, 1996). On the other hand, gouaches have greater proportion of binder to pigment than it is found in transparent watercolours, so gouache produces a continuous paint film of diverse thickness over the paper. Micro-FTIR analyses of the binding media shows the presence of polysaccharides (Fig. 3) that is compatible with the composition of gum arabic used for gouache painting because of its excellent water-solubility (Ormsby et al., 2005). Sorolla performed the sketches with a refined technique based on simple brushstrokes predominantly applied in monolayers (Fig. 4a) or multilayers ways (Fig. 4b). It can also be seen the presence of complex mixtures of pigments as shows a dark area of the sketch V28 (Fig. 4c), where some pigments were identified by microanalysis: bone black, Prussian blue, lead white, zinc yellow, vermillion and hearth pigments. The opacity of gouache allowed Sorolla to rectify and rework images and details to get the desirable effect but with the drawback of applying a thick pictorial (multi)layer that could produce evident signs of

Table 2
Identified pigments in the Sorolla's sketches for the “Vision of Spain” from the Hispanic Society of America collection.

Sketch	Type	Lead White	Zinc White	Calcium based white	Red Ochre	Vermillion	Chrome Yellow	Zinc Yellow	Yellow Ochre	Chromium Oxide / Viridian	Scheele's Green/ Emerald Green	Green Earth	Prussian Blue	Ultramarine	Cobalt blue	Earth Pigments (Siena)	Earth Pigments (Umber)	Bone Black	Carbon Black / Organic
V28		X				X		X	X	X			X			X		X	
V29		X				X			X	X				X		X		X	
V30	collage		X			X	X		X	X				X		X		X	
V31						X				X				X				X	
V32		X				X			X							X		X	
V33		X				X			X			X		X		X		X	
V33P		X														X		x	
V34		X			X				X			X		X		X		X	X
V35		X							X			X		X		X		X	X
V36		X														X		X	
V37		X			X				X			X				X		X	
V38		X				X												X	
V39				X															X
V40	collage	X				X	X		X			X	X			X		X	
V41		X				X	X		X	X			X			X		X	
V42	collage	X				X			X				X	X		X		X	
V43		X				X			X	X				X		X		X	X
V44		X				X			X	X				X		X		X	
V45		X				X			X	X						X		X	
V46		X				X			X	X				X		X		X	
V47	collage	X	X			X			X		X			X		X		X	
V48	collage	X					X							X					X
V49	collage	X	X			X		X		X	X			X		X			X
V50	collage	X	X			X	X		X	X	X		X			X			X
V51	collage	X	X			X	X	X	X	X	X		X			X	X	X	
V52	collage	X				X	X			X	X			X	X	X		X	X
V53	collage	X	X			X	X			X	X		X			X		X	X
V54	collage	X				X				X			X			X		X	
V55	collage	X	X			X			X			X	X			X		X	X
V56	collage		X			X					X					X		X	
V57	collage		X							X	X		X					X	
V58	collage	X				X			X	X	X		X			X			X
V59		X								X			X			X		X	

cracking and flaking (Larsen, 2015).

No preparation or priming layers have been detected and the gouache pigments were applied directly on the paper surface. Sorolla used papers of different quality and texture that present a wide range of brownish tones due to the presence in different proportions of inert mineral charges, mainly natural earths (iron oxides), calcium compounds, silicon and barite. Fig. 5a shows the EDXRF spectrum of the paper used in the sketch V36 where the above mentioned elements are identified. This spectrum will be considered as representative of all the analysed papers.

3.2. *White pigments.*

The most frequently white pigment used by Sorolla in the sketches of the *Vision of Spain* is *lead white* (lead carbonate: $2PbCO_3 \cdot Pb(OH)_2$). This pigment was detected and identified pure or in mixture with other pigments to obtain different levels of chromatic saturation lightening the hue of the colours in accordance with the amount of added lead white. A characteristic EDXRF spectrum of lead white can be seen in Fig. 5b associated to a dress of a woman from the sketch V28. Sorolla also used zinc white (zinc oxide: ZnO) and only in one sketch (V39) calcium based white pigment. Zinc white as pure pigment is identified in some analysed points as is shown in the EDXRF spectrum from the sketch V57 presented in Fig. 5c. The kind of the white pigment used as pure or mixed with other pigments varies from one sketch to another. For example, Sorolla utilized exclusively lead white in the sketch V37, zinc white in the sketch V57, and both white

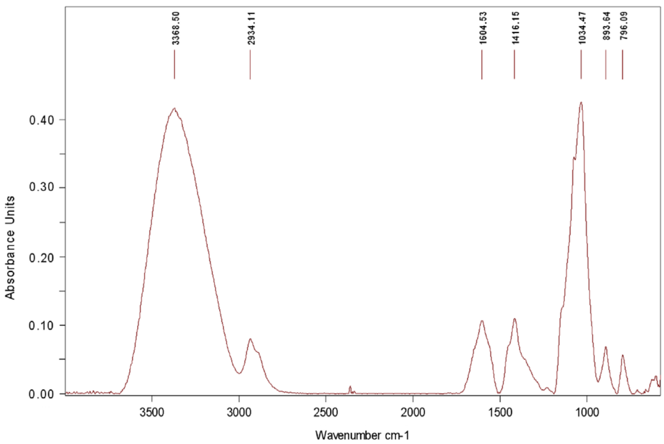

Fig. 3. Micro-FTIR spectrum of the gouache binder media showing the IR bands of polysaccharides (gum arabic).

pigments (lead white and zinc white) in the sketches with a collage of figures as in the sketch V53. EDXRF spectra of the pure *lead white* and pure *zinc white* pigments did not show fluorescence peaks emission of other elements suggesting that, in the paint formulation used by Sorolla, no extenders were added to the white pigments.

3.3. *Red and orange pigments*

In this series of ketches Sorolla opted for the use of *vermillion* (HgS) as the main red pigment. The presence of vermillion is evident by intense fluorescence peaks of Hg as is shown in the EDXRF spectrum of the Fig. 5d that corresponds to a red clothing from the sketch V43. Sorolla also used iron based red pigments (*red ochres*, Fe_2O_3), sometimes as pure red pigment and sometimes mixed with vermillion or other pigments to introduce some variety into shades of red. Vermillion is also used to adjust the shade of flesh tones (carnations) and to obtain pink tones. Zones with orange coloration are not frequent in the sketches and the orange colour was obtained with a mixture of red and yellow pigments; for example, vermillion and chrome yellow in the sketch V29, or vermillion and ochre yellow in the sketch V46.

SEM-EDX analysis of the micro-samples obtained from white and red colour areas are in concordance with EDXRF analysis and identify the presence of lead white, zinc white, vermillion and red ochre.

3.4. *Yellow pigments*

EDXRF measurements of yellow areas indicated the presence of three different yellow pigments. The most frequently used is *yellow ochre* ($Fe_2O_3 \cdot H_2O$). A second yellow pigment was characterized by the presence of zinc, chromium and potassium in its spectra (Fig. 5e), suggesting the use of *zinc yellow* ($4ZnO \cdot 4CrO_3 \cdot K_2O \cdot 3H_2O$). A third yellow pigment detected in the sketches is a lead-chrome based pigment, probably *chrome yellow* ($PbCrO_4$). These three types of yellow pigments were identified by SEM-EDX in accordance with EDXRF analysis. As example, Fig. 6 shows the positive identification of chrome yellow by SEM-EDX and backscattered electron image obtained from a micro-sample from the sketch V40. This figure shows the characteristic needle-like or rod-like morphology of lead chromate structures (Townsend, 1992; Otero et al., 2012) and their elemental composition (Pb and Cr as key elements and other elements probably related with an earth-based pigment). The darkening or browning of chrome yellow has been reported and needs to be taken into account during the restoration and conservation processes (Kühn and Curran, 1986; Monico et al., 2011). The absence of cadmium, cobalt, strontium and barium on the yellow zones exclude the presence of yellow gouache pigments based on these elements.

3.5. *Green pigments*

There are different types of green pigments in the sketches of the Vision of Spain. Some green coloured areas present high intensity fluorescence peaks of chromium that can be ascribed to the use of chromium based green pigments: *chromium oxide* (Cr_2O_3) or *viridian* ($Cr_2O_3 \cdot 2H_2O$). Other green coloured zones revealed a combination of arsenic and copper, compatible elements with the use of *Scheele's green* ($Cu[AsO_2]_2$)) or *emerald green* ($Cu[C_2H_3O_2]_2 \cdot 3Cu[AsO_2]_2$). Figs. 5f and g, show EDXRF spectra of the green pigment from the sketch V46, characterized by the presence of Cr and the green pigment from the sketch V50, characterized by the presence of Cu and As. In these cases it is not possible to differentiate between chromium oxide and viridian or between emerald green and Scheele's green by means EDXRF spectrometry. On the other hand, in a significant number of green areas were detected the presence of chromium, lead and iron suggesting the use of *chrome green*, pigment obtained by the precipitation of Prussian blue on chrome yellow (Kühn and Curran, 1986). Finally, we can refer the probable use in green zones of a *green earth* pigment, a mixture of hydrosilicates of Fe, Mg, Al and K.

Sorolla used the green pigments individually or mixed with other pigments to obtain different colour shades. Therefore, the attribution of a colour to a pigment in basis of the detected elements by EDXRF can be a challenge, particularly if the painted area is the result of a mixture of pigments. Supplementary measurements on micro-samples from green zones by other analytical techniques that provide information about the molecular composition of the pigments would be necessary to clarify these ambiguities. SEM-EDX analyses of samples from green pigments are not appropriate to solve the ambiguity in their identification. Optical microscopy images allow us to observe in some samples from green zones the presence of greenish-blueish grains. The needle-like shaped structures present in the SEM images of this grains and

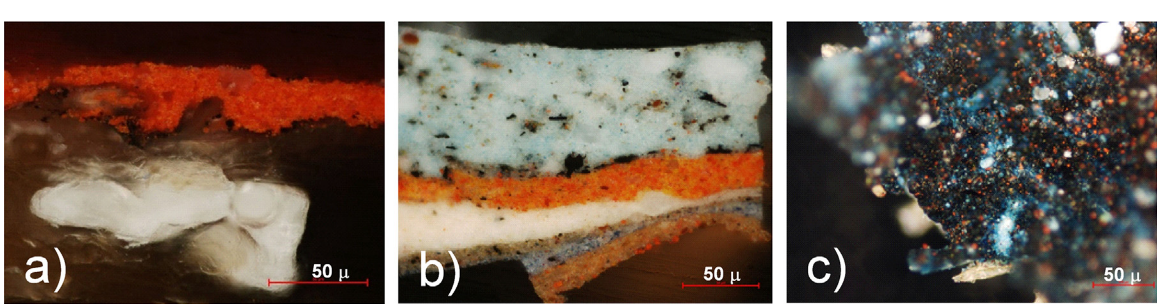

Fig. 4. (a) monolayer of vermilion over the paper from the sketch A1526 (OM 500 ×); (b) stratigraphic view of a multilayer area of the sketch A1524/2 (OM 500x); (c) complex mixture of pigment from a dark zone of the sketch A1520 (OM 200 ×). See text for details.

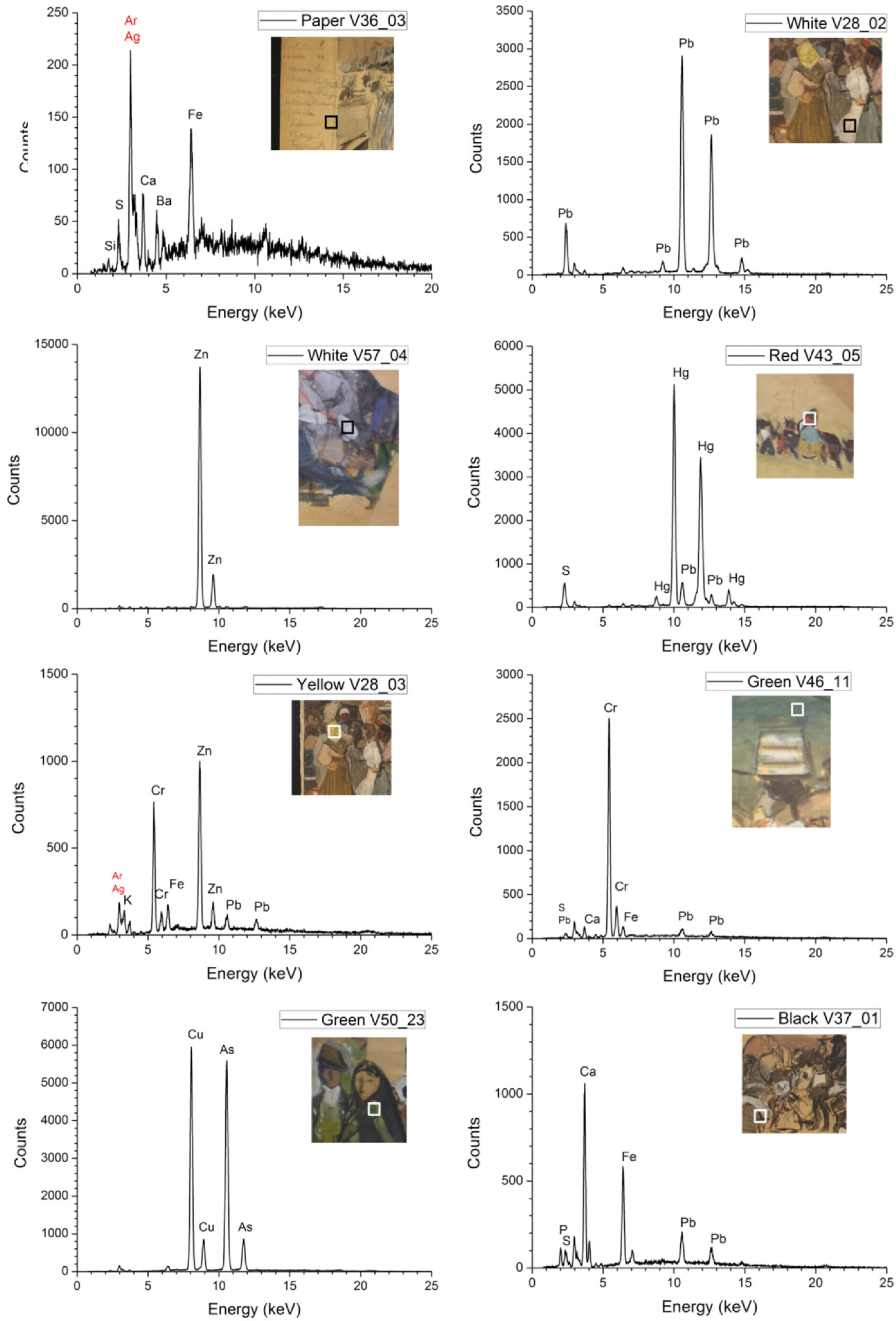

Fig. 5. EDXRF spectra of: (a) the paper of the sketch V36; (b) a white pigment present in the sketch V28 and identified as *lead white*; (c) *zinc white* pigment used in the sketch V57; (d) red pigment (*vermillion*) present in the sketch V43; (e) *zinc yellow* pigment from the sketch V28; (f) a chromium based green pigment (*chromium oxide/Viridian*) in the sketch V46; (g) a copper-arsenic based green pigment *(Scheele's green/Emerald green*) present in the sketch V50; (h) bone black pigment from the sketch V37. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

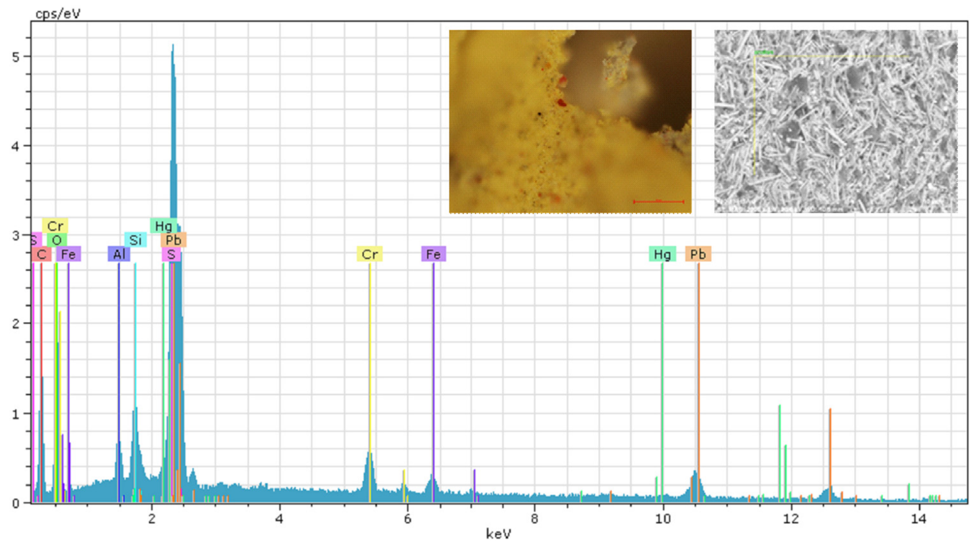

Fig. 6. Optical image (500 ×), SEM-EDX analysis and backscattered electron image of the chrome yellow pigment present on the sketch V40. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

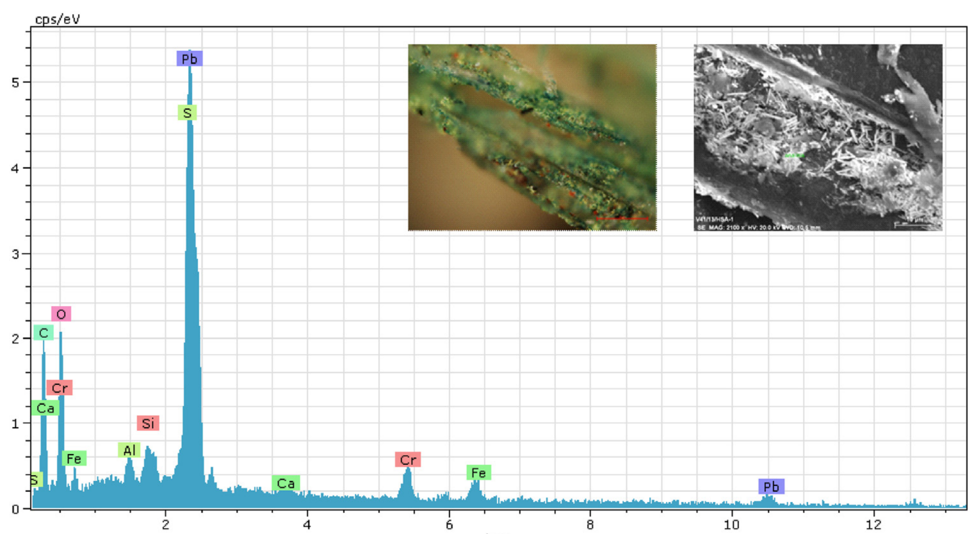

Fig. 7. Optical image (500 ×), backscattered electron image and SEM-EDX microanalysis of a mixture of lead chromate yellow and Prussian blue pigment from a yellow zone of the sketch V41. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the detection of iron, chrome and lead in the EDX spectra (Fig. 7) is compatible with the use of a mixture of lead chromate yellow and Prussian blue to achieve the green pigment in the sketch V41.

3.6. Blue pigments

The nature of the blue pigments used in the sketches is not obvious. The detected elements in blue zones are lead, with its omnipresent fluorescence lines, and iron, with medium or low intensity fluorescence lines. There are no lead based blue pigments and therefore the most probable candidate is the *Prussian blue* ($Fe_4[Fe(CN)_6]_3$) (Berrie, 1997), but the paper under the pigment contains mineral charges in form of natural earths and then it is difficult discern whether the iron signal correspond to the blue pigment or to the paper support. Moreover, the composition of the blue pigments would correspond to an *organic blue* or to a synthetic *ultramarine* ($Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$), in which case their elemental composition (light elements) is difficult to detect by EDXRF. The situation is complicated if we consider the possibility that an organic blue or ultramarine blue would be mixed with earth pigments. On the other hand, cobalt was only detected in the blue pigments of the sketch V52, but the EDXRF spectra of the blue pigments from the rest of the sketches reveals the absence of cobalt fluorescence peaks, so we rejected the use of cobalt based pigments except for the sketch V52. Likewise, copper is absent in all the analysed blue coloured areas and we also rule out the use of copper based blue pigments.

Therefore, the probable pigments used by Sorolla in his work were Prussian blue, ultramarine synthetic and organic blue, but their identification requires other analytical techniques in a similar way as we have indicated in the discussion of the green pigments. Synthetic ultramarine and Prussian blue have been unambiguously identified from samples analysed by SEM-EDX. The microanalysis of the ultramarine pigments, one of them is showed in Fig. 8 from a light blue area of the sketch V30, indicated the presence of sodium, aluminium, silicon and sulphur, elements that characterizes this pigment. The SEM-EDX microanalysis of the Prussian blue used in the sketches showed the characteristic element combination for ferric ferrocyanide mixed with white pigments. Fig. 9 shows the microanalysis of the Prussian blue pigment

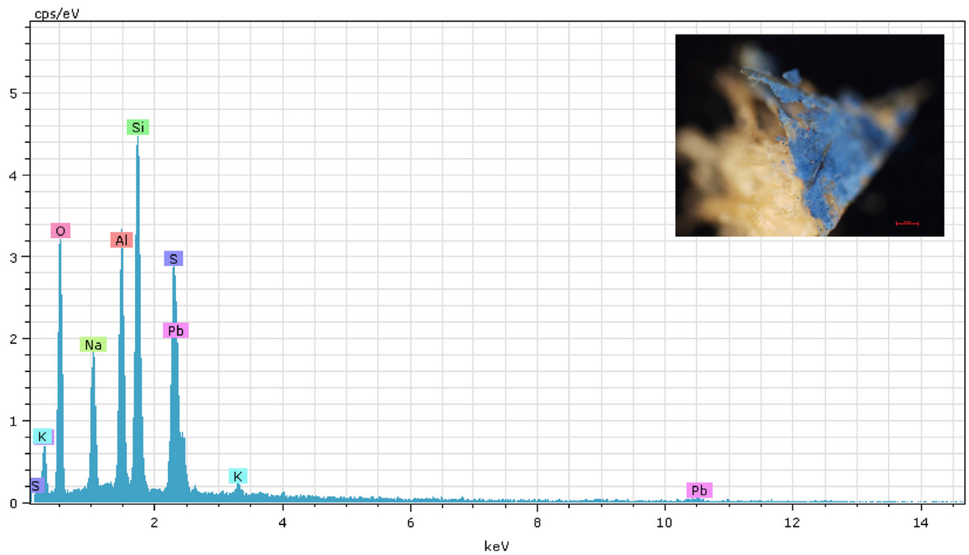

Fig. 8. Optical image (500 ×) and SEM-EDX microanalysis of the ultramarine synthetic pigment from the sketch V30.

used in the sketch V29 that includes fluorescence peaks of lead and iron and where we can see an electron backscattered image of Prussian blue particles surrounded by finely divided rounded particles of lead white (Gettens et al., 1993). Organic blue pigments are not evident in the cross sections, EDXRF and SEM-EDX analyses and they could have been used mixed with other pigments in zones with undefined coloration.

3.7. Brown pigments

Brown colorations are iron based pigments from a variety of *ochres* (*natural and synthetic earth pigments*). Owing to the presence of iron as the basic component of these pigments, it is not possible to distinguish between different types of ochre (iron oxides, iron hydroxides) by EDXRF with the exception of the *umber* pigments, characterized by the presence of Mn and Fe in the EDXRF spectra. These ochre shades play an important role in the mixtures with other pigments to obtain the flesh tones of the figures or to obtain a green-brownish colour. Sorolla probably also used organic brown pigments that we have not been able to identify by EDXRF.

3.8. Black pigments

Black coloured zones in the sketches present EDXRF spectra with intense fluorescence lines of phosphorous and calcium, elements associated with the use of *bone black (or ivory black)* ($Ca_3[PO_4]_2$) as can be seen in the fluorescence spectrum of a black pigment from the sketch V37 (Fig. 5h) and in the SEM-EDX microanalysis of a black pigment from the sketchV36 (Fig. 10). On the other hand, some of the black coloured zones that appear in the sketches correspond to complex mixtures that contain, among others, vermillion, umber or zinc yellow (Fig. 4c). In monochrome sketches as V39, Sorolla only used black pigments and the absence or very weak presence of calcium in these sketches is compatible with the use of carbon based black pigments as lamp black and/or charcoal. In these cases, no differences between the EDXRF spectra from a black painted zone and the unpainted paper has been

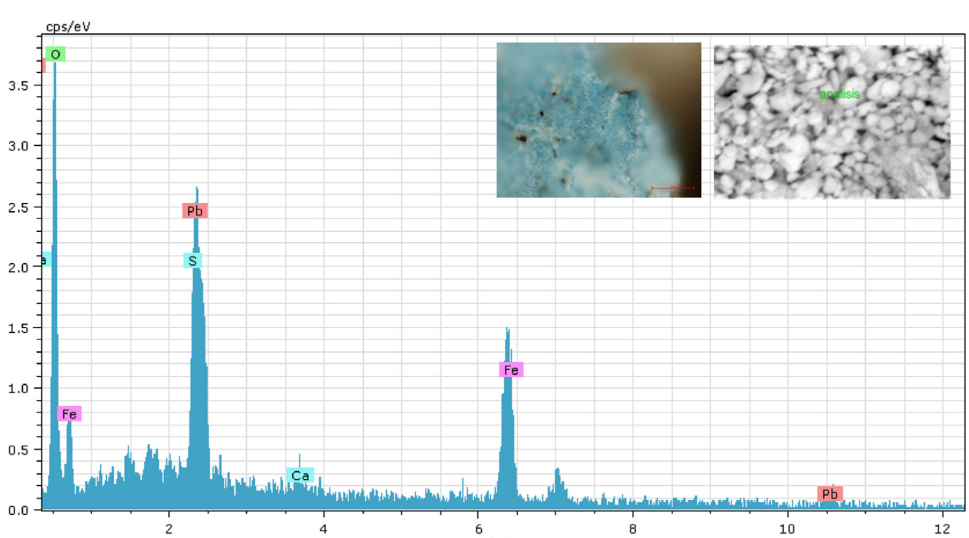

Fig. 9. Optical image (500 ×) and SEM-EDX microanalysis of a mixture of Prussian blue and lead white present in a blue pigment of the sketch V29. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

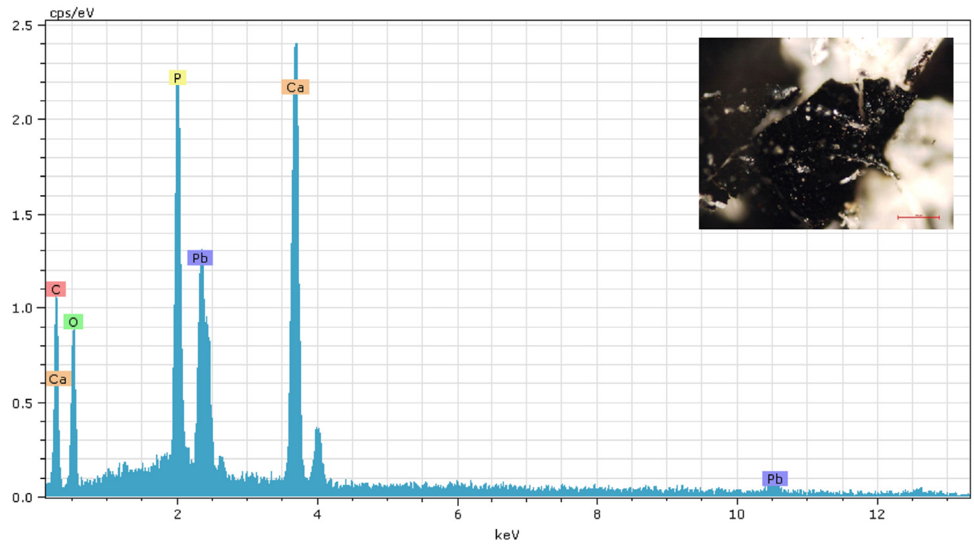

Fig. 10. Optical image (200 ×) and SEM-EDX microanalysis of a bone black pigment present in the sketch V36.

observed because of the fact that carbon cannot be detected by EDXRF spectrometry operating in an atmosphere of air (López-Montalvo et al., 2014). The preparatory drawings of some figures as the woman of the sketch V43 were done by means of a carbon based (charcoal) pigment. Sometimes, Sorolla used bone black pigments and carbon black pigments in the same sketch.

4. Conclusions

EDXRF analysis together with SEM-EDX and micro-FTIR analysis have been used for the characterization of the gouache pigments and materials used by Joaquín Sorolla in the preparatory sketches of the Vision of Spain. The combination of these analytical techniques revealed a lot of valuable information that will be used to assist curators, restorers and art researchers of the Sorolla's pictorial production.

With regard to the identification of gouache pigments, the comparison of the non-destructive results with those obtained by microsampling shows a remarkable agreement. The characteristic of the Sorolla's palette in these gouache paintings is the systematic use of some pigments such as the lead white, pure or mixed with other pigments in the paint layers; the vermillion in deep red areas, carnations and flesh tones; the bone black or ivory black in clothes, shadows and contour lines; the chromium based green pigments of the landscapes; the ultramarine used in the skies; and the yellow ochre and earth pigments used in the landscapes, clothes or skin tones of animals and persons. Zinc white, chrome yellow and copper–arsenic based pigments are predominantly detected in the sketches that are made out of pieces/figures of painted paper juxtaposed and pasted on another paper (collages). In these cases, Sorolla only used one kind of pigment (white, red, yellow, blue or green) on each piece of the collage. The non-destructive analysis carried out in this study by means of portable EDXRF spectrometry was suitable for the identification of all the above mentioned pigments with the exception of lakes, carbon based pigments and organic pigments. Chromium based green pigments (chromium oxide/viridian) and copper–arsenic based green pigments (Scheele's green/emerald green) cannot be differentiated by EDXRF because it is an elemental analytical technique.

Finally, we can conclude that the protocol for the analytical study of the gouache pigments used by Sorolla in the preparatory sketches of the Vision of Spain is appropriated to go any more deeply into the knowledge of the Sorolla's palette. First, we have made a preliminary in situ analysis by means of non-destructive EDXRF spectrometry to make an extensive characterization of the painting materials obtaining significant information on the elemental composition of the pigments and their distribution on the surface of the paint. Secondly, a selective sampling was carried out to answer to the outstanding questions that the EDXRF is unable to solve. In this case, the analysis of cross sections from micro-samples provides essential information about the painting technique, arrangement of the pigment layers, and microscopic structure and composition of the pigments.

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