ISSN: 2230-9926

Available online at http://www.journalijdr.com

IJDR

International Journal of Development Research
Vol. 07, Issue, 12, pp.17835-17845, December, 2017

ORIGINAL RESEARCH ARTICLE OPEN ACCESS

DIFFERENTIATION BLACK PIGMENTS IN "*MAJA AND CELESTINA*", A PAINTING ON ALABASTER BY FRANCISCO DE GOYA

***[1]Luis Rodrigo Rodríguez-Simón, [2]Miguel Ángel León- Coloma and [3]Vicente del Sol-López**

1PhD. Department of Paint and Restoration, Faculty of Fine Arts, University of Granada, Av. Andalucía nº 38, 18071 Granada, Spain
2PhD. Department of Historical Heritage, Faculty of Humanities, University of Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain
3Proffesor, Department of Languages and Computer Systems, University of Granada, Periodista Daniel Saucedo Aranda s/n E-18071, Granada, Spain

ARTICLE INFO

Article History:
Received 26th September, 2017
Received in revised form
22nd October, 2017
Accepted 08th November, 2017
Published online 30th December, 2017

Key Words:
Francisco de Goya, 18th century,
Painting, alabaster support,
Vine black pigment, lamp black pigment,
Scanning Electron Microscopes (SEM-EDX),
micro Raman spectroscopy (mRS),
Visible and near-infrared spectrophotometry.

ABSTRACT

Identifying and characterising the pigments forming part of a work of art is particularly relevant for the chronological authentication of a painting, as well as knowledge of the great masters artistic resources, which could result in the work being catalogued. The aim of this research is to morphologically characterise and differentiate two black pigments of an organic nature, which are intrinsically mixed together and compacted by a binder. These pigments are part of a black monochrome painting on alabaster by Francisco de Goya. The observation with SEM and EDX microanalysis have allowed to identify and morphologically differentiate these two pigments: vegetable black or vine black and carbon black (lamp black). Thus, in the case of vine black pigment, polygonal forms were observed that may indicate the rigid walls characteristic of vegetable cells. Lamp black pigment can be associated withsmall spherical structures, apparently homogeneous, which appear along with the polygonal vine black forms. We have suggested that Goya mixed these two pigments to obtain a more stable pictorial mixture provided by the black vine pigment and a darker color by the lamp black pigment. The two black pigments that were identified are bound together by a mixture of linseed oil and egg, denoting a tempera grassa painting technique.

Highlights

- This study is based on a painting done on a translucent alabaster plate.
- Alabaster is a little used material as support in paintings, although it has been very used in sculptures, altarpieces and covers.
- This painting reproduced an original pictorial composition by Goya, using only the colour black.
- This innovative study proposes the morphological differentiation of vine black and lamp black pigments.
- Both pigments are mixed and bound together forming a single colour.
- The morphological differentiation of vine black and lamp black pigments has been undertaken based on original paint samples from an 18th century painting by Francisco de Goya
- Via SEM-EDX it has been possible to morphologically differentiate vine black and lamp black pigments based on the cellular structure of the former and the amorphous structure of the latter.

Citation: Luis Rodrigo Rodríguez-Simón, Miguel Ángel León- Coloma and Vicente del Sol-López, 2017. "Differentiation black pigments in "*maja and celestina*", a painting on alabaster by francisco de goya", *International Journal of Development Research*, 7, (12), 17835-17845.

INTRODUCTION

Identifying the components present in works of art constitutes a research activity that has been being developed for several decades (Gettens *et al*., 1966; Plester, 1966) because of interest in finding out about the artistic materials and painting techniques used by artists in the creation of their works.

Historiographical and technical precedents

These raw materials and painting methods have been passed down throughout history in ancient manuscripts and treatises, which have been compiled in specialist literature (Merrifield, 1967). Even the methods and material used by the grand masters have reached us today (Eastlake 2011). In addition, writings about different pigments and painting practice have been preserved (Cennini, 1968; Leonardo da Vinci, 1995; Vasari, 1960; Armenini, 2000; De Holanda, 2003;Pacheco, 1990; Palomino, 1988) and even formulas and formularies with prescriptions detailing the ingredients and the preparation of compounds (Gheroldi, 1995). Furthermore, there is a large amount of literature that gathers detailed descriptions of techniques, painting materials and their use in Art (Doerner, 1989; Mayer, 1985; Bazzi, 1965; Laurie, 1967; Thompson, 1956). Other authors dedicate their work to the specific study of pigments and binders (Gettens and Stout, 1966; Montagna, 1993; Harley, 2001; Berrie, 2001). All these precedents have encouraged an interest in knowing works of arts internally, applying examination methods and analytical techniques for the purpose of obtaining the maximum possible information about the usual materials and methods of the different painting schools introduced by the great masters, thus acquiring a deep understanding of their style and technique, of their hallmarks and peculiarities. All these technical details will serve to authenticate previously anonymous works of art, or reject those works of doubtful authorship. It is therefore vitally important to recognise pigments and clarify the creative process based on a stratigraphic interpretation of samples and a detailed observation of the painting's surface (density or fluidity of the pictorial paste, graphics, texture and thickness of brushstrokes, superposition of layers, location and distribution of pigments etc.) (Rodríguez Simón, 2011, 2015).

Current approaches to knowledge of materials and artistic methods

There is now regular research being carried out based on examination methods and analytical and spectroscopic techniques for studying and researching works of art. The aim is to identify the artistic materials present in the great paintings, as is the case of pigments and binders, and determine the peculiarities each artist may have in the manner of using pigments. One example would be the mixture of vermilion and red lead with cochineal lacquer used to achieve the red of a Madonna's tunic (Rodríguez Simón, 2015). This approach is comparable to the study of the use of black pigments in the painting we are dealing with. The mixture of different types to achieve a single colour black could constitute a peculiarity of the Aragonese painter. The scientific techniques that are systemically applied to the study and research of Artworks can be classified as examination methods, based on electromagnetic radiation and on analytical and spectroscopic techniques. The examination methods are: X Rays (XR), Infrared Reflectography (IR), Scanning Multispectral IR Reflectography and Ultraviolet Fluorescence (UV). The most used analytical and spectroscopic procedures are: Optical Microscopy with transmitted and reflected illumination (OM), Scanning Electron Microscopes (SEM-EDX) and Transmission Electron Microscopes (TEM), X Ray Diffraction (XRD), Raman spectroscopy (RS) and micro Raman spectroscopy (mRS), Visible and near-infrared spectrophotometry, Gas Chromatography-Mass Spectrometry (GC-MS). By means of this equipment it has been possible to identify artistic materials, of an organic and non-organic nature, present in works of art. This is achieved by interpreting the corresponding spectrum and chromatograms obtained from each one of these instrumental techniques. In the case of SEM-EDX and XRF micro-analysis it is possible to identify the pigments and materials used as a base via their constituent chemical elements, captured in the corresponding spectrum (Spring, 2004, 2007; Favaro *et al*. 2012). Raman Spectroscopy also obtains spectrums with bands and peaks characteristic of each pigment, based on its direct application onto the surface of the work and also on each layer of the corresponding transverse sections (Civici *et al*. 2005; Nevín,2008; Muralha *et al*., 2012; Gutiérrez-Neira *et al*., 2013; Pozzi *et al*., 2014; Frano *et al*., 2014).

Identification of black pigments of an organic nature. Objectives, limitations and scope

In the case of black pigments with an inorganic composition, such as black lead oxides and manganese oxides, their identification can be carried out by means of the above analytical and spectroscopic techniques. These pigments are recognised via the corresponding spectrum and their constituent chemical elements, as well as their characteristic bands and peaks (Lahlil *et al*., 2012;Rampazzi *et al*., 2007). Literature also exists on identifying the black pigments present in cave paintings (Chalmin *et al*., 2006; Vázquez *et al*., 2008; Jezequel *et al*., 2011; Eastaugh *et al*., 2004). In relation to black pigments of an organic nature, it is possible to identify them through SEM-EDX as they all have Carbon as a main element. Through this micro analytical technique, as has been shown, these pigments are recognised based on the chemical elements they are composed of, including Carbon, (Rodríguez Simón *et al*., 2011; Tomasini *et al*., 2012a, 2012b, 2015). However, when the black pigments form part of a painting it is difficult to characterise them, at both a structural and a molecular level, based on stratigraphy. In this sense some experiments have been carried out using Raman Spectroscopy to identify black pigments based on carbon, taking actual pigments as a reference (Tomasini *et al*., 2012a, 2012b; Coccato *et al*., 2015). The representative peaks have then been compared to artistic samples in order to identify the black pigments present, taking into account the similarity between their characteristic Raman bands (Tomasini *et al*., 2015).

The objective of this study is to carry out a methodological test on the differentiation of black pigments of an organic nature forming part of a work of art, either in isolation or mixed with other pigments. We proposed evaluating their possible discrimination taking into account the morphological aspects related to their internal structure, above all when pigments are combined, forming a single colour for the entire pictorial composition, as occurs in this work by Goya. We there for proposed a multi-analytical approximation through the following techniques: SEM-EDX, mRS, Visible and near-infrared spectrometry, Optical microscopy and Gas chromatography/mass spectrometry. This article presents a

discussion about the limits and scope of the different methods in characterising black pigments of an organic nature. Recognising these black pigments is complicated in works of art where dark colours predominate and even in other works that are done solely with this colour, achieved with a single black pigment or with a mixture of two or more. Our case study is a monochrome painting in which only the colour black predominates. It is achieved with the mixture of lamp black and vine black; pigments that we have been able to identify with SEM-EDX. However, it has not been possible to differentiate between them or identify their location and distribution in the pictorial strata as they form a uniform and continuous layer, compacted by the binder. We therefore proposed differentiation these black pigments through complementary non-destructive analytical techniques, given the small size of the work, such as Raman Spectroscopy (Rodríguez Simón *et al*.,2012) and Visible Spectrometry-near Infrared (Rodríguez Simón *et al*., 2013). These techniques did not produce any results that we could consider conclusive. They have been unable to help us differentiate between and individually characterise the different types of black present in the painting being studied, which were previously recognised with SEM-EDX.

With the aim of furthering our research and taking as a reference Cennino Cennini's descriptions of *different ways of making black (*Cennini, 1968, 5, chapters XXXVI and XXXVII) and also the experiments of Winter (Winter *et al*., 2007; Tomasini *et al*., 2012a, 2012b, 2015) and those of Gettens and Stout (Gettens *et al*., 1966), we propose undertaking an analysis of the micro samples extracted from the work studied, utilising the dramatic enlargement provided by the Scanning Electron Microscope, as described in the section on Materials and Methods. This technique has enabled us to observe characterise and differentiate between these two black pigments based on their molecular structure, together with their micro analytical identification. Taking into account the writings of Cennino Cennini (Cennini, 1968 –5),and the works of Montagna and (Montagna, 1993; Eastaugh, 2004), this study indistinctly records the black pigments studied as, on the one hand, vegetable black or vine black obtained by burning vine shootsor wood; and on the other hand, carbon black or lamp black made by roasting mineral oil and also by burning linseed oil, coal, pitch, resins or waxes.

MATERIALS AND METHODS

Brief description of the painting: *Maja and celestina* by Francisco de Goya (Rodríguez Simón, 2013) (Figure 1), in particular collection, is a painting done on a translucent alabaster plate with dimensions of 18.8 x 155cm and a thickness of 16 mm. It is a monochrome painting in which only varying intensities of the colour black are perceived in the form of different fluid or opaque brushstrokes applied to the surface, depending on the luminosity and chiaroscuro of the composition. Goya also plays with burin incisions in order to delimit the forms and accentuate areas of greater luminosity.

Materials Samples

The materials employed within this study are as follows:

A stratigraphy of the painting, prepared from a microsample encased in methacrylate resin.

Figure 1. Maja y Celestina by Francisco de Goya. Photograph of the painting (18.8 cm x 15.5 cm)

A small amount of powder from the painting, by a brushstroke running along the edge of the alabaster.

Analytical Techniques

These materials have been observed and analysed via the following techniques:

Scanning electron microscopy (SEM Leo 1430 VP) with microanalysis of elements (EDX)applied to the stratigraphy and also to a small portion of black-paint powder, from brushstroke the edge of the work.

Scanning electron microscopy, SEM Leo 1430VP, linked to a system for the microanalysis of elements via energy-dispersive X-ray spectroscopy, Inca 350, version 17 (hereinafter, SEM-EDX). Scanning electron microscopy enables the identification of elements with low atomic numbers, including carbon. Obtaining images of back-scattered electrons (BSE) shows the average atomic number of the pigments, and the images of secondary electrons (SE) provide information on texture and structure, whilst analysis of the elements making up the pigments is undertaken via energy-dispersive X-ray spectroscopy (EDX). The SE and BSE images and analysis via energy-dispersive X-ray spectroscopy were acquired at an acceleration voltage of 20 Kv. The spectra were acquired over 50 seconds, with a resolution of 20 ev/Ch and an acquisition rate of 3000cps.

Confocal micro-Raman spectroscopy [mRS], applied "in situ", focusing the laser directly on to the surface of the work and also on the stratigraphy prepared via a microsample of the painting. Raman spectra were obtained employing a an InVia Raman microscope (Renishaw) with a Raman signal acquisition geometry of 180º (backscattering), a 50x lens (numerical aperture of 0.75) and attenuating filters between

0.1% and 0.05% of maximum laser strength, the output power being 20 mW. The equipment was fitted with a Leica DM LM microscope, connected to a video camera, with a holographic notch filter to eliminate Rayleigh dispersion, a 1200 L/mm diffraction grating and a 400 x 575 pixels CCD-type detector. Excited lines of both 514.5 and 785 nm in a diode laser were employed to analyse these types of pigment. Raman analysis was carried out on the stratigraphy and also directly on the work. The confocal properties of the equipment enable us to place the painting directly under the objective lens of the microscope connected to the spectrometer, allowing us to carry out non-destructive in situ analysis.

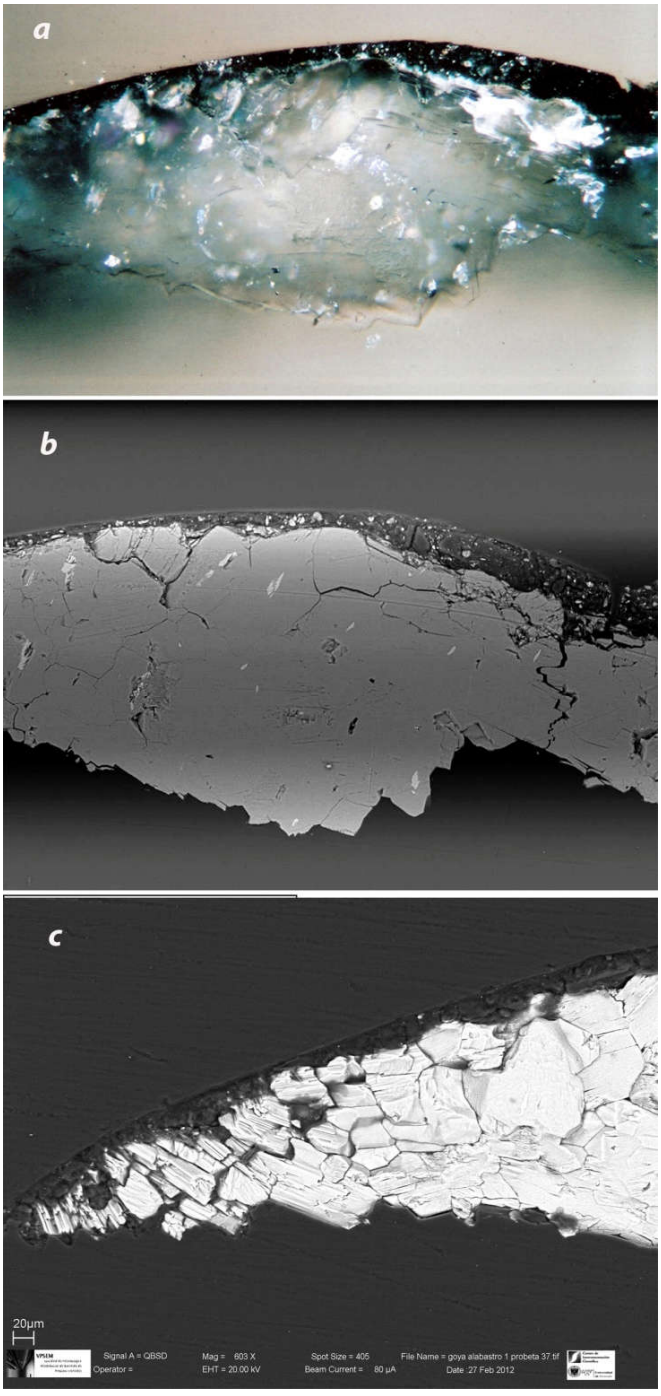

Figure 2a. Photograph obtained by Optical microscopy Figures 2b, 2c. Photograph obtained via scanning electron microscopy of the stratigraphy extracted from the painting, shown Pictorial layer and under strong magnification, wherein it is possible to distinguish the gypseous structure of the alabaster that serves as a medium (figure 2c)

Visible and near-infrared spectrometry, applied "in situ" on to the surface of the picture.

The spectrophotometric data was collected using an Ocean Optics USB2000+ spectrometer with a Labsphere integrating sphere, 8º/h geometry (specular component included) with 5/16 inch sample port diameter. A voltage stabilized 7Watt tungsten-halogen lamp (mod. HL-2000-FHSA) optimized from 360-2000 nm range was used together with Spectralon diffuse white (99% reflectance) as reflectance standard.

Other instrumental techniques

Optical microscopy is used in order to observe the stratigraphy or transverse section of the painting. Preliminary examination of the painting samples was carried out, on the one hand, via a polarised light optical microscope, with parallel and crossed nicols (Carl Zeiss, Jenapol U model). On the other hand, an ultraviolet microscope was employed (Olympus, CX41RF model) affording information on the fluorescence given off by the pigments and binding agents. The information provided by the optical microscope is essential for recognising the internal micro structure resulting from the creative process followed by the painter, which is vitally important for authenticating the work. It also allows the microscopic image to be visualised with the sequence of strata and the actual colours of the constituent pigments of each one of the layers, their distribution, milling and texture. With ultraviolet illumination it is possible to better distinguish the stratigraphic structuring due to the fluorescence emitted by both pigments and binders.

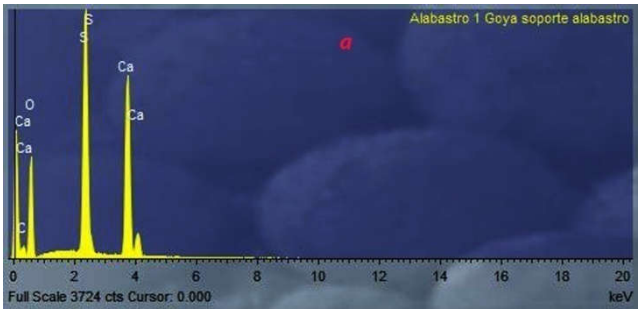

Figure 3a. Spectrum obtained via SEM-EDX microanalysis, with the characteristic peaks of gypsum that makes up the alabaster medium.

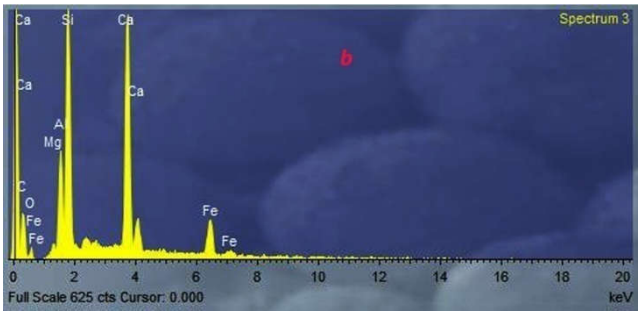

Figure 3b. Spectrum obtained via SEM-EDX microanalysis, with the characteristic peaks of calcium carbonate and the mix of calcium and magnesium carbonate, secondary components of the gypsum, in its alabaster form, and also silicates originating from clays, which are normally natural contaminants of gypsum

Gas chromatography/mass spectrometry. It is undertaken based on micro samples extracted from the pictorial surface.

This technology enables identification of the binding agents that provide cohesion to the pigments, allowing us to determine the painting technique.

The samples were treated with Meth-Prep II to detect oils, resins and waxes. In the case of carbohydrates and proteins, hydrolysis and subsequent derivatisation via silylation with TBDMSTFA in pyridine was employed.

RESULTS AND DISCUSSION

Analysis with optical microscope

Analysis of this monochrome painting by Goya was carried out, firstly, via a single stratigraphy (Figures 2a, 2b, 2c) that, under the optical microscope, provided us with information on the internal structure and the sequence of layers of which it is composed: an initial layer, corresponding to the alabaster medium, and two further superficial layers that make up the black paint layer.

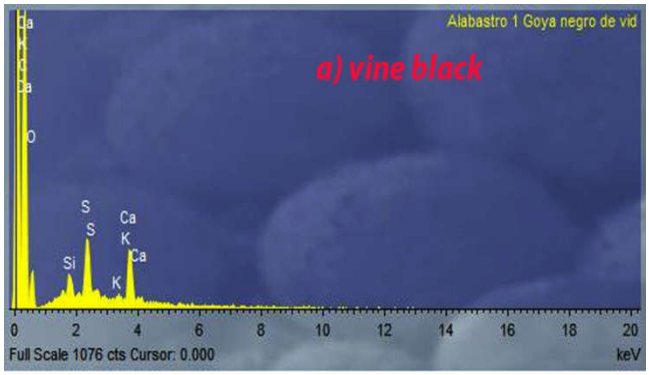

Figure 4a. Spectrum corresponding to the vine black pigment, with the characteristic peaks of carbon, and potassium and calcium as a trace element.

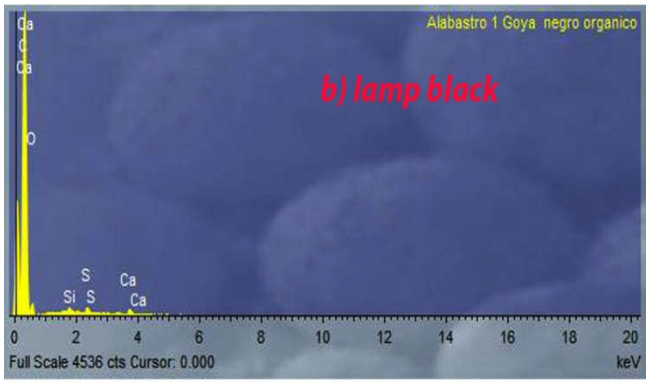

Figure 4b. Spectrum corresponding to the carbon black pigment, with its characteristic peak

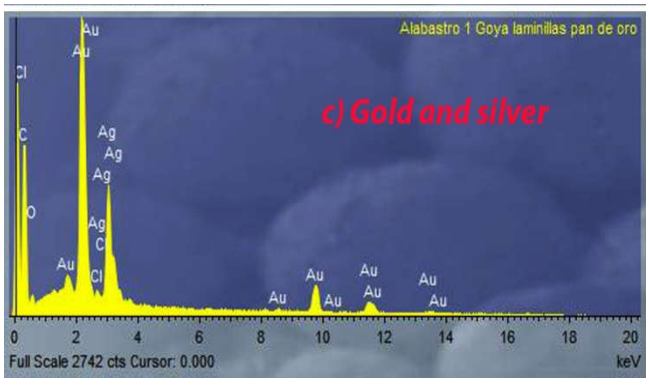

Figure 4c. Spectrum corresponding to the small flakes of gold leaf included within the mix of the two black pigments, with its characteristic peaks, which illustrate the purity of the gold.

In some areas, depending on the fluidity and intensity of the brushstrokes, there is only a thin stratum, but in others there are two overlapping layers which are denser and more opaque. The latter is the case of the intense black of the room's rear wall, against which the figures of *Maja and Celestina* are silhouetted, applied by the painter to give depth to the scene.

Analysis of the stratigraphy via SEM-EDX

EDX microanalysis enabled us to identify *calcium sulphate* as the main component (Figure 3a), *calcium carbonate and a mix of calcium and magnesium carbonate* as secondary components of the gypsum, given its alabaster form, and also *silicates* originating from clays, which are natural contaminants of gypsum (Figure 3b). These components confirm the gypseous nature of the material employed as a medium. The painting layers of this cross-section also revealed the presence of carbon black (lamp black), vine black or vegetable black, gold, quartz and earth as pigments employed by Goya to create the work. Identification (Rodríguez Simón *et al*., 2011) was carried out on the basis of the chemical elements present in spectra captured with SEM-EDX spectra (Figures 4a, 4b, 4c).

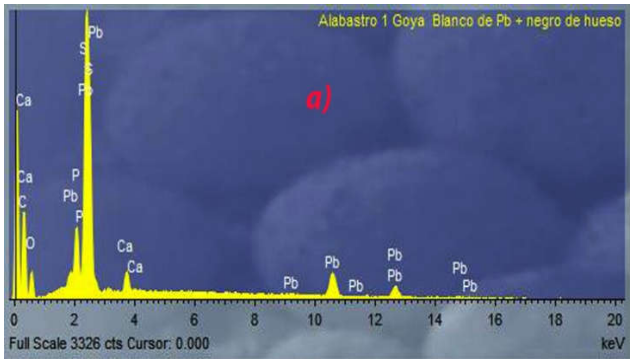

Figure 5a. Spectrum showing the characteristic peaks of lead white and bone black pigments that were found to be present in the painting at a trace level

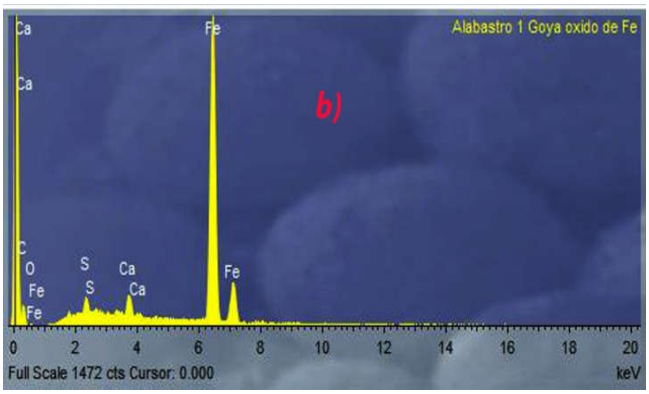

Figure 5b. Spectrum corresponding to the black pigment made up of iron oxides, detected by a high iron peak

SEM-EDX observation under high magnification

However, in this study our aim is to make advances in the differentiation of these two black colours, which are mixed together within the painting, proving difficult to distinguish via SEM-EDX, as carbon is the main component in each case. Therefore, to identify them via microanalysis when employing this instrumental technique, we must make recourse to the identification and detection of trace elements within the existing pigments, such as potassium, and calcium, which is

characteristic of vine black or vegetable black (Charcoal), minor elements present in plant cells. (Montagna, 1993; Tomasini, 2012) (Figure4a). Our aim is to study these black pigments taking as a reference their morphological differentiation based on the experiments of Winter and Tomasini, (Winter *et al*., 2007; Tomasini, 2012a, 2012b, 2015) - 42,43, 45, 49), using as a tool the dramatic enlargements made possible by the Electron Microscope to visualise the materials selected in our research, which are detailed in the section on Materials and Methods: stratigraphy and black powder from a brushstroke on the edge of the alabaster. The stratigraphy and the small particles of black powder were duly prepared for observation with an electron microscope. It is these that have enabled the two black pigments; vine black and lamp black to be characterised and differentiated.

We have suggested that the painter mixed the two black pigments in order to obtain a more stable colour. Therefore, the two samples were studied in detail under high magnifications, whilst simultaneously undertaking the microanalysis associated with this technique, with the aim of verifying the characterisation of the internal particles. In each case, the characteristic elements of the pigments were identified, revealing themselves to be *lamp black*, *vine black or vegetable black (Charcoal) and gold*. Oxygen peaks have also been detected in the corresponding spectra. The presence of oxygen was indicative of oxidized compounds arising from incomplete combustionof wood by fire (Tomasini *et al*., 2012). Moreover, both the stratigraphy and powder extracted from the painting contained fragments of other black pigments, such as *bone black*, *lead white* and iron oxides (Figures5a, 5b).

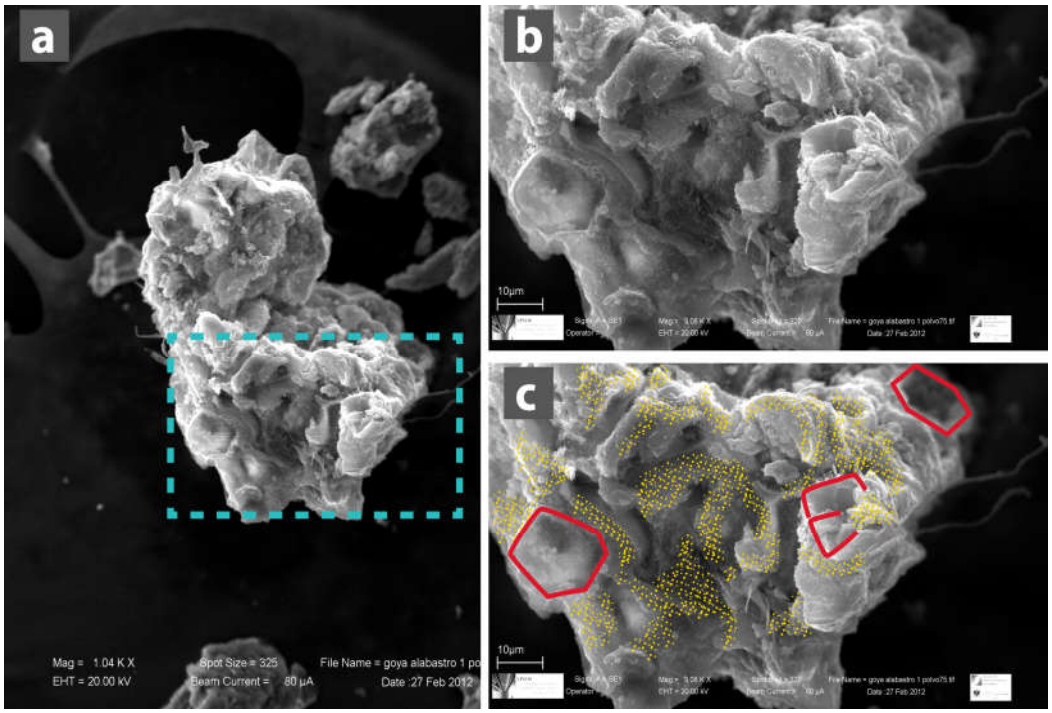

Figure 6a-6b-6c. Detail 1: Polygonal forms that, in our view, indicate the rigid walls characteristic of vegetable cells from vine black pigment. This Polygonal configurations covered by spherical structures, made up of very small particles, enveloping the entire ensemble and which may be ascribed to the amorphous structure of carbon black pigment (lamp black)

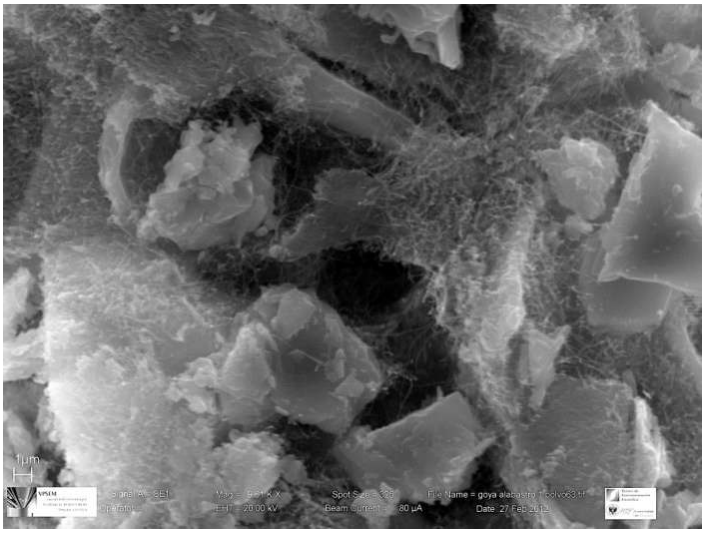

Figure 7. Observation of the mix of vine black and lamp black pigments under high magnification. Polygonal shapes characteristic of the walls of plant cells are observed and also and also tiny spherical structures linked by the binders are observed

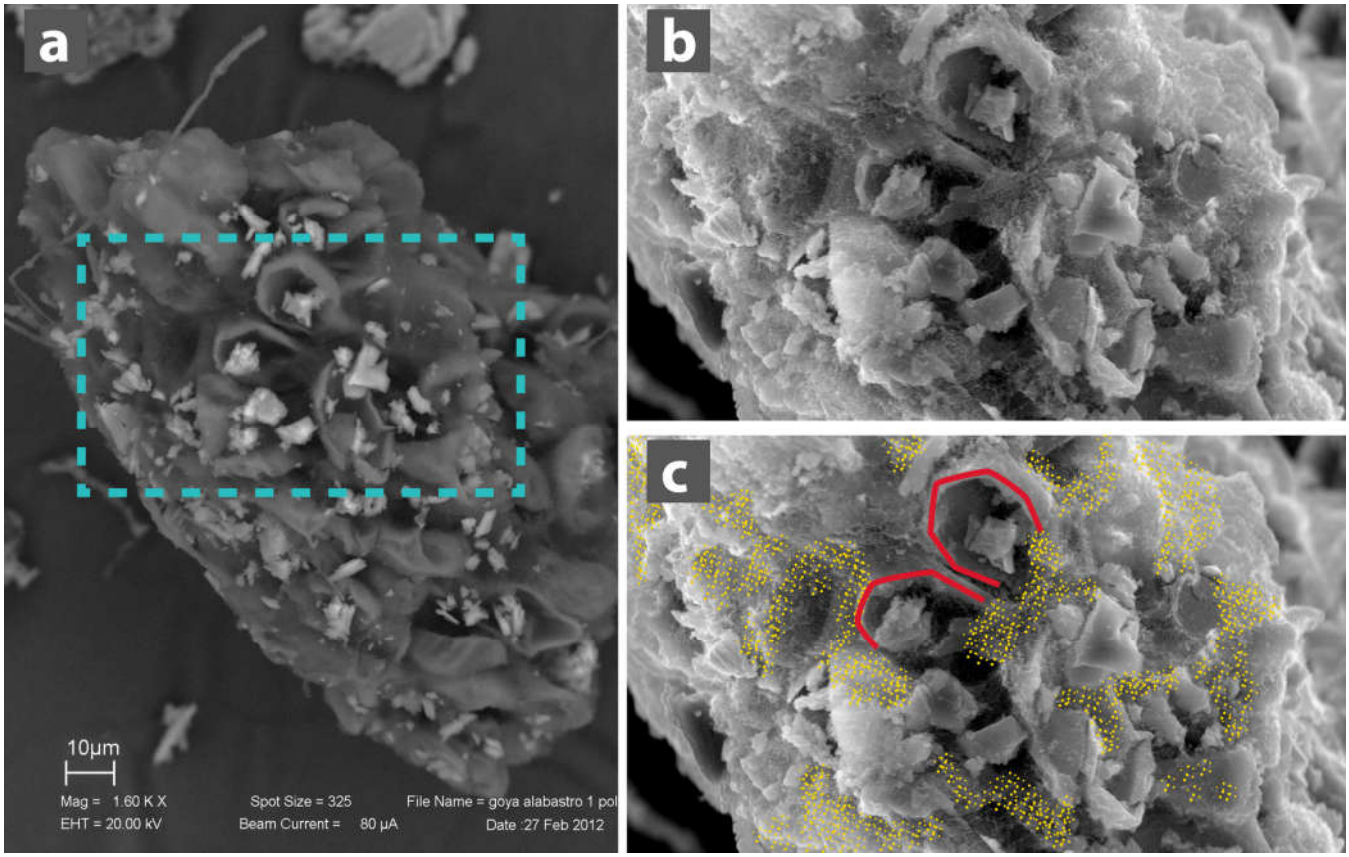

Figure 8 - a,b,c.- Polygonal forms that, in our view, indicate the rigid walls characteristic of vegetable cells from vine black pigment. This Polygonal configurations covered by undefined formations made up of very small particles, which are deposited on the configurations, enveloping the entire ensemble and which may be ascribed to the amorphous structure of carbon black pigment (lamp black)

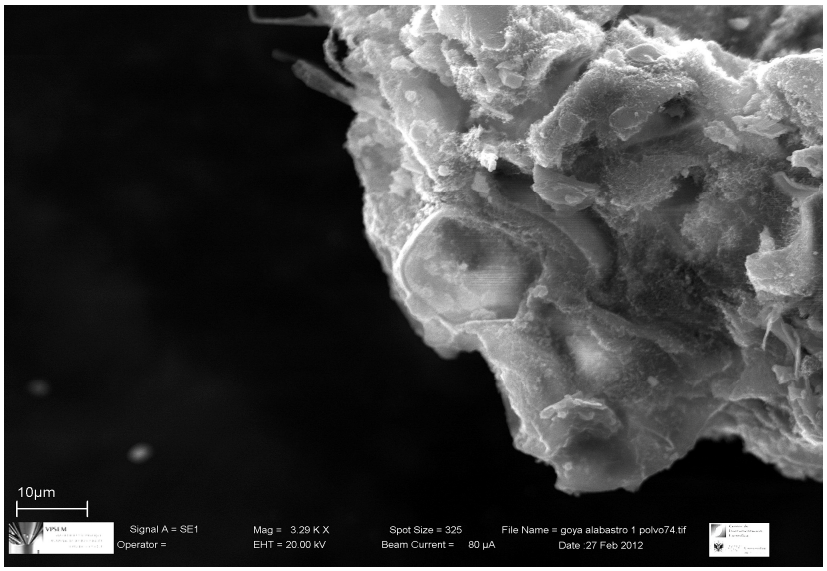

Figure 9.Observation of the mix of vine black and carbon black pigments under high magnification. The silhouette of the rigid wall characteristic of plant cells has been observed.

We suggest that the presence of traces of lead white and bone black pigments could be considered as additives, adulterations or contaminations of the brush or the palette. We have also thought that these iron oxides detected with SEM-EDX are of black color, since, in the observation of the cross-section with optical microscopy, no iron oxide particles of red color nor of iron oxides of yellow color have been detected. However, based on this premise, we suggest that mix of lamp black and vine black with a view to obtaining a more stable colour: carbon black provides a strong colour, but it has It has a weak consistency derived from its origin, acquiring a greater degree of solidity when mixed with vine black, which is more consistent due to the rigid structure of the cell walls of the wood, a pigment that does not offer the same capacity to blacken. This reflection could be related to Tomasini's comment to about the presence of iron detected in the referenced samples of vine black: the presence of iron may be related to the addition of iron oxides to obtain a dark-colored

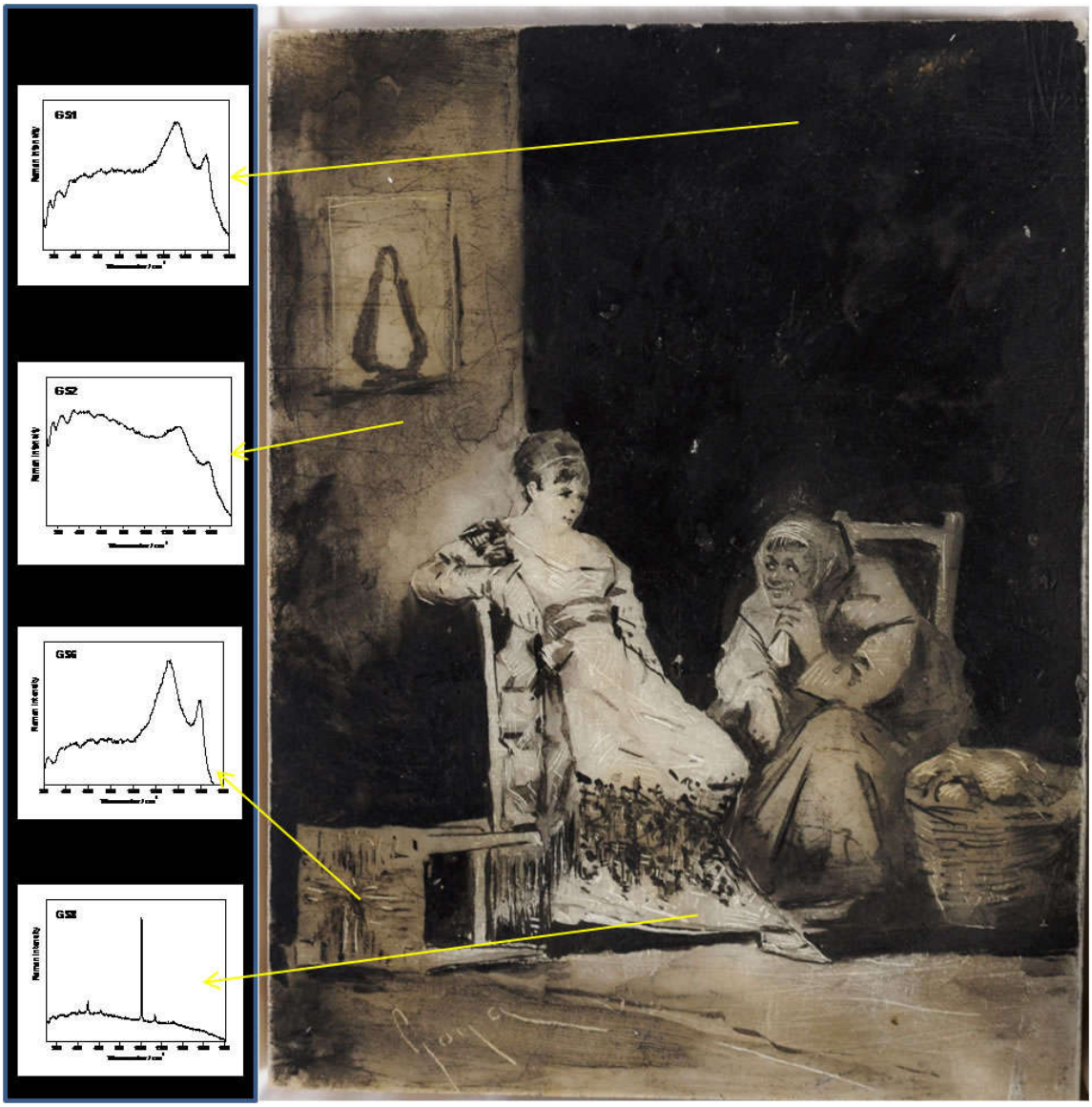

Figure 10. Photograph of the painting "Maja y Celestina", indicating the points on the surface of the painting at which Raman microspectrometry analysis was carried out, showing the corresponding spectra with arrows, wherein the three spectra at the top correspond to carbon and the three at the bottom, to the gypsum of the alabaster.

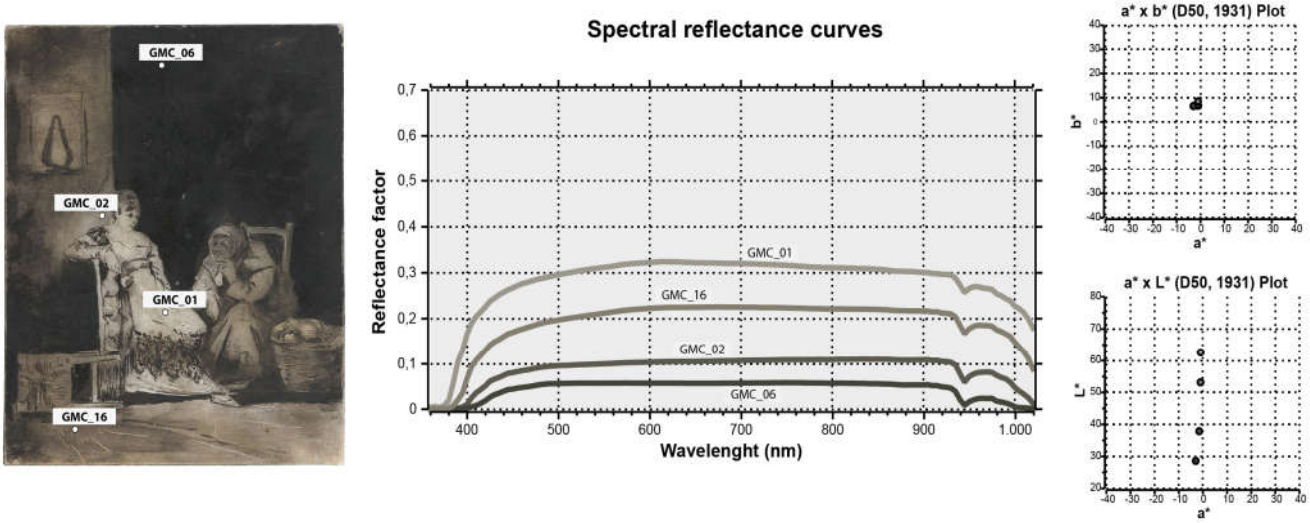

Figure 11. Measurements of spectral reflectance in different areas of work, taken *in situ* on the surface of the painting

material (Tomasini *et al*., 2012). This approach could justify the presence of iron peaks in the spectra captured by SEM-EDX in the paint object of our study. When observing the stratigraphy under high magnification, the two pigments in question could not be distinguished at a morphological level, given the cohesion between the pictorial strata brought about by the binding agent, compacting the mixture in such a manner that we were unable to visualise the existence of structures at an internal level. Nevertheless, as indicated above, analysis of the samples via SEM-EDX enabled us to identify the characteristic chemical elements associated with each pigment, as shown in the corresponding spectra. However, the sample entailing powder from brushstroke from the painting enabled us to characterise the two pigments on the basis of their morphology, as high magnification has uncovered structures that has made differentiation viable. Thus, in the case of the vine black pigment or vegetable black, polygonal forms were observed that may indicate the rigid walls characteristic of vegetable cells, given its botanical origin. (Figure 6a, 6b, 6c). SEM-EDX confirmed the presence of Carbon as a major element and potassium and calcium, a trace element that characterises vegetable or vine black (Montagna, 1993) (Figure 4a), are expected to derive from plant material (Tomasini *et al*., 2012). This Polygonal configurations are mixed by spherical structures, apparently homogeneous, made up of very small particles, which are deposited on the polygonal forms, enveloping the entire ensemble and which may be ascribed to structure of carbon black pigment (lamp black) (Figure 7). These corpuscles may be due to the spherical structurewith smooth surfaces of the lamp black pigment (Tomasini, 2012; Winter *et al*., 2007) Figure 8a, 8b, 8c, and Figure 9). SEM-EDX indicated a high carbon peak in the corresponding spectrumby their high content of carbon (Rodríguez Simón *et al*., 2011; Tomasini *et al*., 2012) (Figure 4b).Furthermore, in the two samples (stratigraphy and powdered paint), observation under high magnification enabled us to morphologically verify the presence of minute gold leaf flakes (Rodríguez Simón *et al*., 2011) that are included within the two pigments in question: golden particles that have been identified via SEM-EDX as gold of a very high purity.

Raman analysis

Analysis of the stratigraphy was also undertaken employing a complementary technique for pigment identification:

Raman spectroscopy, which failed to provide conclusive results in terms of the differentiation of these colours. Raman spectroscopy analysis was undertaken "in situ", focusing the laser directly on to the surface of the painting, selecting different points on the basis of the degree of transparency and the intensity of the colour:

- Focused on intense black.
- Focused on a more translucent hue.
- Focused on the ash coloured base coat applied before the painting was commenced.
- Focused on a clear area where the white of the alabaster comes to the fore.

In the three spectra captured from different intensities of the black colour, the bands that characterise carbon can be observed (1340w and 1595vs cm^{-1}) (Pagés-Camagna*et al*., 2007); and in the fourth spectrum we observe an intense band of approximately 1000 cm^{-1} which characterises gypsum (alabaster), along with bands of 494 and 1136 cm^{-1} (Figure 10). As Tomasini points out, these results are characteristic bands of carbon. Nevertheless, it is very difficult to discriminate the sourceof carbon-based pigments because their Raman spectra are very similar, although differences in band positions, intensities, and bandwidths may be observed after a detailed study of the spectra. The stratigraphy was also analysed via application of the Raman laser at 514.5 nm and 785 nm., again capturing the spectra corresponding to carbon and alabaster.

Analysis via visible and near-infrared spectrometry

As with Raman Spectroscopy, the analyses with Visible-near Infrared Spectrometry were carried out *in situ*, applying the colorimeter directly onto the surface of the work, choosing those points that presented a different degree of intensity in the brushstroke colour, ranging from a translucent tonality to an intense black. The aim was to confirm the similarity or difference between the spectral bands captured in each one, and be able to determine the characterisation of lamp black and vine black pigments, using non-destructive methods. This is similar to the experiments on a Roman fresco wall paint dated around 30 BC (Gatta *et al*., 2012) carried out by Gatha and collaborators (2012). These authors suggest that thermogravimetry and differential thermo analysis techniques (TG-DTG) are useful for authenticating black powder pigments, but also that an old black pigment could only be identified *in situ* with Colorimetry. In our case, Spectral reflectance measurements obtained in different samples of the work show spectral curves between 360 nm and 1020 nm without characteristic traces. The peak observed at 922 nm is a peak within the transmission of the fibre optic employed. Both the form of spectral distribution and the a* b* coordinates of the different samples present similar values, and seem to correspond to a mixture of several black pigments rather than matching one specific pigment (Gatta *et al*., 2012) (Figure 11).

Identification of binders

The identification of binders has been done by Rodríguez Simón and Parra Crego through Gas Chromatography-Mass Spectrometry. The following results were obtained:

The peaks that appear in the chromatogram corresponding to the analysis of fatty acids correspond to azelaic, palmitic and stearic acids, with a Palmitic/Stearic proportion of 1.67 and an Azelaic/Palmitic of 0.2. These values indicate the characterisation of a drying oil such as linseed. Other minor components are also recognised such as traces of pine resin and beeswax. In relation to the binders of a protein nature, the analysis of amino acids from the whole sample indicates the determination of animal glue due to the presence of hydroxyproline and a high percentage of glycine. In addition, a second analysis of the insoluble residue detected a significant increase in amino acids such as glutamic acid and aspartic acid, indicating the existence of egg albumen (Rodríguez Simón *et al*., 2011). The presence of these peaks in the corresponding chromatograms suggests that the binder would be made from a mixture of linseed oil and egg. The animal glue comes from impregnating the alabaster in order to limit its porosity and prepare it for receiving the layers of paint.

Conclusion

The recognition, identification and characterisation of pigments present in an artistic sample, as well as their

arrangement, location, distribution and proportion in the sequence of layers forming part of the internal structure of a painting, is crucially important for assigning a chronology to the work in question and for cataloguing it within a specific painting school. We've experimentedalso that the combination of the different analytical techniques used has not facilitated the definitive characterisation of the black pigments of an organic nature, as they are bound together forming a consistent pictorial mass. Because of this difficulty, we suggest evaluating their possible discrimination on the basis of the morphological differences found in the dramatically enlarged images captured by the scanning electron microscope, bearing in mind the cellular aspects related to their internal structure. This is particularly important in this case as the pigments are combined, forming a single colour black. This is the reason for starting from a minute quantity of small particles of black powder from a brushstroke on the edge of the alabaster, which has given us the possibility of characterising and differentiating the black pigment of an organic nature present in this painting by Francisco de Goya. Thus, with the dramatic enlargements achieved with the scanning electron microscope, in the case of the vine black pigment we have observed some polygonal forms that could indicate the rigid wall characteristic of vegetable cells. The lamp black pigment can be connected to the smallest particles with spherical structures. These appear bound to the polygonal forms of vine black, or vegetable black as a result of these two pigments having been intrinsically mixed with the binder. This latter aspect shows the need for the samples to be magnified with an electron microscope, due to the minute size of the powder particles obtained from the brushstroke on the edge of the alabaster. Gold leaf particles, within the mix of blacks, were also observed, indicating the painter's aesthetic intention to give luminosity and brilliance to the intense black predominating in certain areas of the work. The chemical information obtained on the materials and technology used in the manufacture of the paintings contributed to increase our knowledge on about the paintings by Francisco de Goya.

Acknowledgements

Andalusian Research Groups HUM-839. Analyses were performed in the Scientific Instrumentation Centre (CIC) of the University of Granada (Spain).

REFERENCES

Armenini, G.B. 2000. *De los verdaderos preceptos de la pintura*. Madrid: Visor Libros.

Bazzi, M. 1965. *Enciclopedia de las Técnicas Pictóricas*. Barcelona-Madrid: Noguer.

Berrie, B. H. 2001. *Artists' Pigments. A Handbook of Their History and Charasteristics*. Vol.4. London: Archetype Publications.

Cennini C. 1968. *The Craftsman's Handbook "Il Libro dell'Arte"*. New York: Dover Publications Inc.

Ciatti, M. and Brunetti, B.G. 2012. *Caravaggio's Painting Technique*. In Proceedings of the CHARISMA workshop. Firenze: Nardini Editore, Kermesquaderni.

Civici, N., Demko, O., Clark, R.J.H. 2005. Identification of pigments used on late 17th century Albanian icons by total reflection X-ray fluorescence and Raman microscopy. *Journal of Cultural Heritage*, 2005, 6: 157-164.

Coccato, A., Jehlicka, J., Moens, L., Vandenabeele, P. 2015. Raman spectroscopy for the investigation of carbon-based black pigments. *Journal Raman Spectroscopy*, 46: 1003-1015.

Chalmin, E., Vignaud, C., Salomon, H., Farges, F., Susini, J., Menu, M. 2006. Mineral discovered in Paleolithic black pigments by transmission electron microscopy and micro-X-ray absorption near-edge structure. *Applied Physics A* 83: 213-218.

De Holanda, F. 2003. *De la pintura antigua y El diálogo de la Pintura*. Madrid: VisorLibros.

Doerner, M. 1989. *Los materiales de pintura y su empleo en el Arte*. 5ª ed. Barcelona: Reverté.

Eastaugh N, Walsh V, Chaplin T, Siddall R. 2004. *Pigment Compendium: A Dictionary and Optical Microscopy of Historic Pigments*. Oxford: Elsevier Butterworth-Heinemann.

Eastlake, C.L. 2001. *Methods and materials of painting of the Great Schools and Masters*. New York: Dover PublicationsInc.

Favaro, M., Guastoni, A., Marini, F., Bianchin, S., Gambirasi, A. 2012. Characterization of lapis lazuli and corresponding purified pigments for a provenance study of ultramarine pigments used in Works of art. *Anal Bioanal Chemistry*, vol. 402: 2195-2208- DOI: 10.1007/s00216-011-5645-4.

Frano, K.a., Mayhew, H. E., Svoboda, S. A., Wustholz, K.L. 2014. Combined SERS and Raman analysis for the identification of red pigments in cross-sections from historic oil paintings. *Analyst*, 139: 6450-6455.

Gatta, T., Campanella, L., Coluzza, C., Mambro, V., Postorino, P., Tomassetti, M., Visco, G. 2012. Characterization of black pigment used in 30 BC fresco Wall paint using instrumental methods and chemometry. *Chemistry Central Journal* 6 (Suppl 2): 52.

Gettens, R. J., and E. W. FitzHugh. 1066. Azurite and blue verditer. *Studies in Conservation*, 11: 54-61.

Gettens, R.J. and Stout, G. 1966. *Painting Materials*. New York: Dover Publications Inc.

Gheroldi, V. 1995. *Ricette e Ricettari. Tre fonti per la storia delle tecniche delle arti alla Biblioteca Queriniana di Brescia (sec. XVI-XVII)*. Brescia: Comune di Brescia.

Gutiérrez-Neira, P.C., Agulló-Rueda, F., Climent-Font, A., Garrido, C. 2013. Raman spectroscopy analysis of pigments on Diego Velázquez paintings. *Vibrational Spectroscopy*, 69: 13-20.

Harley, R.D. 2001. *Artists' Pigments c. 1600-1835*. London: Archetype Publicationes.

Hofmann, M. 2008. Il Mellon Digital Documentation Project. I dieci quadri di Rafaello della National Gallery di Londra. *Kermes*, 2008, 72: 25-27.

Jezequel, P., Wille, G., Bény, C., Delotme, F., Dean-Prost, V., Cottier, R., Breton, J., Duré, F., Despriee, J. 2011. Characterization and origin of black and red Magdalenian pigments from Grottes de la Garenne (Callée moyenne de la Creuse-France): a mineralogical and geochemical approach of the study of pehistorical paintings. *Journal or Archaeological Science*, Elsevier, 38 (6): 1165-1172.

Lahlil, S., Lebon, M., Beck, L., Rousselière, H., Vignaud, C., Reiche, I., Menu, M., Paillet, P., Plassard, F. 2012. The first in situ micro-Raman spectroscopic analysis of prehistoric cave art of Rouffignac St-Cernin, France. *Journal Raman Spectroscopy*, 43:1637-1643.

Laurie, A.P. 1967. *The Painter's Methods and Materials*. New York: Dover Publications Inc.

Leonardo da Vinci. 1995. *Tratado de la Pintura*. Madrid: Ediciones Akal.

Mayer, R. 1985. *Materiales y técnicas del Arte*. Madrid: Hermann Blume.

Merrifield, M. 1967. *Medieval and Renaissance Treatises on the Arts of Painting*. New York: Dover Publications Inc.

Montagna, G. 1993. *I pigmenti. Prontuario per l'arte e il restauro*. Firenze: Nardini.

Muralha, V.S.F., Burgio, L., and Clark, R.J.H. 2012. Raman spectroscopy analysis of pigments on 16-17th c. Persian manuscripts. *Spectrochimica Acta Part A,* 92: 21-28.

Nevin, A. Loring Melia, J., Osticioli, I., Gautier, G., Colombini, M.P. 2008. The identificacion of copper oxalates in a 16th century Cypriot exterior wall painting using micro FTIR, micro Raman spectroscopy and Gas Chromatography-Mass Spectrometry. *Journal of Cultural Heritage*, 9:154-161.

Pacheco, F. 1990. *El Arte de la Pintura*. Madrid: Cátedra.

Pagés-Camagna, S.,Duval, A., Guicharnaud, H. 2004. Study of Gustave Moreau's black drawings: identification of the graphic materials by Raman microspectrometry and PIXE, *J. Raman Spectroscopy*, 35, 628-632.

Palomino, A. 1988. *El museo pictórico y escala óptica. Práctica de la pintura*. Madrid: Aguilar Maior.

Plester, J. 1966. Ultramarine, natural and artificial. *Studies in Conservation*, 11: 62-91.

Pozzi, F., Jan van den Berg, K., Fiedler, I., and Casadio, F. 2014. A systematic analysis of red lake pigments in French Impressionist and Post-Impressionist paintings by surface-enhanced Raman spectroscopy (SERS). *Journal of Raman Spectroscopy*, vol. 45 Issue 11-12: 119-1126.

Rampazzi, L., Campo, L., Cariati, F., Tanda, G., Colombini, M.P. 2007. Prehistoric wall paintings: The case of the Domus de Janas Necropolis (Sardinia, Italy). *Archaeometry*, 49: 559-569.

Rodríguez-Simón, L.R. 2011. Maja y Celestina. Una pintura sobre alabastro firmada por Francisco de Goya. El proceso creativo y la técnica de ejecución pictórica. *Kermes*, 84: 37-44.

Rodríguez-Simón, L.R. 2013. Maja y Celestina. Una nueva pintura sobre alabastro en el catálogo de Francisco de Goya. *Cuadernos de Arte de la Universidad de Granada*, 44: 145-170.

Rodríguez-Simón, L.R. 2015. El proceso creativo y la estructuración estratigráfica como señas de identidad y autenticidad. La pequeña Madonna di Foligno de Rafael, como caso de estudio. *PH INVESTIGACIÓN*, 5: 45-67.

Rodríguez-Simón, L.R., Del Sol López, V., Manzano Moreno, E., Navas Iglesias, N., López-Ramírez, M. R. 2013. Advances in the study of black pigments via spectroscopic techniques in a painting by Francisco de Goya. In: TECHNART 2013. Analytical Spectroscopy in Art and Archaeology, Abstract book, Amsterdam: Rijksmuseum, p. 86.

Rodríguez-Simón, L.R., López-Ramírez, M.R., Navas, N., Manzano, E. 2012. Black pigments identification on alabaster painting: Maja y Celestina by Francisco de Goya, in situ mRS and SEM-EDX analysis. In: IRUG 10 book of abstracts.Barcelona: Universidad de Barcelona, p. 192-193.

Rodríguez-Simón, L.R., Parra Crego, E. 2011. Caracterización de pigmentos y aglutinantes mediante VPSEM y GC-MS en una pintura firmada por Francisco de Goya: Maja y Celestina. En: Heritage and Design of Geometrical Forms. Granada: Universidad de Granada: 385-408.

Roy, A. Spring, M. 2007. Raphael's Painting Technique: In Working practices before Rome. Proceedings of the Eu-ARTECH workshop. Firenze: Nardini Editore, Kermesquaderni.

Spring, M. 2004).*Perugino's Painting Materials*: Analysis and context within sixteenth-century easel painting. In Brunetti, B.G, Seccaroni, C., Sgamellotti, A. (eds). The Painting Technique of Pietro Vannucci, called Il Perugino. Proceediings of the Labs TECH Workshop. Firenze: Nardini Editore, Kermesquaderni, pp. 21-28.

Spring, M. 2007. Raphael's Materials: Some new discoveries and their context within early sixteenth-century painting. In Roy, A. and Spring, M. (eds). Proceedings of the Eu-ARTECH workshop. Firenze: Nardini Editore, Kermesquaderni, pp. 77-86.

Thompson, D. V. 1956. *The materials and techniques of medieval painting*. New York: Dover Publications Inc.

Tomasini, E., Siracusano, G., Maier, M.S. 2012a. Spectroscopic, morphological and chemical characterization of historic pigments based on carbon. Paths for the identification of an artistic pigment. *Microchemical Journal,* 102: 28-37.

Tomasini, E.P., Gómez, B., Halac, E.B., Reinoso, M., Di Liscia, E.J., Siracusano, G., Maier, M.S. 2015. Identificatiion of carbón-based black pigments in four South American polychrome wooden sculpturesby Raman microscopy. *Heritage Science,* 3:19. DOI 10.1186/s40494-015-0049-y.

Tomasini, E.P., Halac, E.B., Reinoso, M., Di Liscia, E.J., Maier, M.S. 2012. Micro-Raman spectroscopy of carbón-based black pigments. *Journal of Raman Spectroscopy*, 43: 1671-1675.

Vasari, G. 1960. *On Technique*. New York: Dover Publications Inc.

Vázquez, C., Maier, M.S., Parera, S.D., Yacobaccio, H., Solá, P. 2008. Combining TXRF, FT-IR and GC-MS information for identification of inorganic and organic components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina). *Anal Bioanal Chem*, 391:1381-1387.

Winter, J., West FitzHugh, E. 2007. Pigments Based on Carbon. In Berrie, B.H. (ed.). *Artists'Pigments: A Handbook of Their History and Characteristics,* Vol.4. London: Archetype Publications, pp. 1-37.

****