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Spectroscopic analysis of roman wall paintings from Casa del Mitreo in Emerita Augusta, Mérida, Spain

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Abstract

The use of visible spectroscopy, applied to chromatic characterization of Roman wall paintings, allows an easy and trustworthy grouping of the samples studied. The use of other spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDS) in conjunction with X-ray diffraction (XRD) allows a good identification of the substances present in the pictorial layers that define and differentiate each chromatic group. In this paper, a study of 40 Roman wall painting samples, from *Pinturas Báquicas* of Casa del Mitreo in Emerita Augusta (Mérida, Spain), is described. In these samples, some pigments of high quality and cost, as well as some unusual mixtures, not described in the bibliography, have been found.

Keywords: Chromatic measurements (CIE64); FTIR spectroscopy; Pigments; X-ray diffraction

1. Introduction

The spectroscopic study of artworks has a great importance because it reveals information that is of general historical interest in the knowledge of artistic materials that were used and available at a certain period, in a particular region and for disseminating new methods. All provides information about the interactions among different cultures and about trade routes. On the other hand, an important purpose of these studies is to help the conservators to determine the deterioration reasons of a certain artwork and optimize the conditions of restoration and conservation.

In this work, 40 Roman mural painting samples from the 2nd century A.D. and in a good conservation state were studied. The samples come from the so-called *Pinturas Báquicas* from Casa del Mitreo in Emerita Augusta (Mérida, Spain). These samples were selected by the restorers of the museum from a 300 plaster fragment set of paintings that showed figurative decorations, plain colors, strips or lines, and are inventoried in the National Museum of Roman Art Collection in that Spanish city. The study of a mural painting sample involves the characterization of the pictorial surface that is constituted of the pigment and

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the substrate in that it is immersed. The chemical composition of both pigment and substrate is responsible for the final color and it can offer substantial information about the techniques that were used in the artwork manufacture.

With this aim, several spectroscopic techniques have been applied for studying the samples, allowing the chromatic characterization and the identification of the pigments that are present.

2. Experimental

All samples have been studied using selected techniques, according to the results of our previous studies [1–5].

2.1. Chromatic characterization

Normally, the chromatic characterization of the pictorial layer is made by means of subjective methods based on the visual comparison between the sample and a table of pre-established colors such as, e.g. the Munsell Code [6,7]. This method can lead to serious errors as it is very much influenced by external factors such as the illumination used during the comparison, the subjective observational abilities of the researcher or the chromatic stability of the patterns used for the comparison.

In this work, an objectively reproducible chromaticity characterization has been carried out using electronic spectroscopy. The method consists of the determination of the optical reflectance within the visible frequency range using an Otsuka MCPD 1100 Visible Ultraviolet Spectrophotometer. The system is equipped with optical fiber light conducting elements that enable the direct study of the pictorial surface of the material to be made without perturbing it.

Using the normalized CIE64 system [7,8], the chromaticity coordinates x_{10}, y_{10} deduced from the tristimulus values X_{10}, Y_{10}, Z_{10} have been calculated. These variables, that define the tonality and the color saturation, have been represented in the color space diagram. An incandescent tungsten lamp with a filtered emission was used as an illumination system and the CIE illuminant was the D_{65} standard source. For the white pattern, a low-pressure compressed tablet of chemically pure magnesium oxide powder was used. The reflectivity of this substance is about 97–98% [9] and it is chemically stable. The sample chamber has a normalized geometry of 0°/45° for the illumination/observation process, in order to minimize the specular/diffuse reflectance ratio of the captured radiation and for obtaining a realistic chromaticity value.

2.2. Chemical analysis

The chemical identification of the pictorial and substrate substances were performed using energy-dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. For obtaining elemental analysis information, a LINK AN10000 energy-dispersive X-ray detector system, joined to a JEOL JSM820 scanning electron microscope, was used. The samples have been gold-coated to prevent surface charging; therefore, a constant gold signal appears in all EDS spectra. Some fragments or chips of about 1 mm^2 have been obtained for observing the pictorial layer.

A Fourier transform infrared spectrometer (Nicolet Impact 410 Spectrophotometer with OMNIC software) has been used to obtain molecular information. The spectral analysis involved the searching of several commercial libraries consisting of 40,000 spectra, including US Geological Survey Minerals, Commercial Material Painter Minerals, Sigma Dyes, Stain and Natural Pigments, Aldrich Condensed Phase and Coating Technology. For making analysis using this technique, the samples have been prepared for the transmittance study grinding little pieces of the pictorial layer with spectroscopic quality potassic bromide that works like a support.

In all cases, the XRD technique was used to confirm the crystal structures of the same molecular compound. In this technique, little pieces without grinding in several mm^2 for destroying the minimum possible surface have been used.

3. Results and discussion

In this work, *mi* is the generic prefix that we have associated to the samples from Casa del Mitreo. A layer, about 1 mm thickness, forms the pictorial surface of all the samples. Calcite, a crystallographic variety of calcium carbonate, was detected in the binder of all the samples along with varying amounts of common impurities that can include quartz, dolomite, etc.

The existence of wax or soap has been ruled out. For that a soxhlet extraction for several samples was carried out. More than 10 refluxes were made using chloroform as dissolvent. The obtained extract was concentrated and the respective infrared spectrum was carried out using a potassic bromide tablet and on it, drops of that solution were being deposited. The spectrum obtained does not indicate the presence of any kind of the aforementioned organic substances.

It has permitted to deduce that the paintings were made using the "fresco painting" technique using lime mortar. Typical components of standard silicates appeared in many cases. These silicates are associated with impurities due to the mortar, dust and burial remains and, only in some cases, to the pigment used for coloring the layer.

The reflectance spectra of the pictorial surface of all the samples have been registered in the visible range over several zones (about 3 mm in diameter illumination spot size) for each of the different samples to obtain a statistically representative value. The colorimetric coordinates x_{10}, y_{10}, Y_{10}, the saturation and the dominant wavelength achieved are shown in Tables 1–3. The chromatic coordinates and the saturation values seem to be very close to the neutral white. This behavior is fitting to the Roman mural paintings [10] because the small concentration of pigments used in the pictorial layer.

The samples appear clearly were grouped into seven zones. The nomenclature used in this paper for designing these groups is based on the human visual sensation of the colors, despite the chromaticity values indicating some small discrepancies. These zones are named as: (1) ocher colors, (2) reddish colors, (3) bluish colors, (4) greenish colors, (5) white colors, (6) gray colors and (7) black colors. The results are described below for each of these groups.

3.1. Ocher colors

This color appears in the *mi*1, *mi*2, *mi*3, *mi*4, *mi*5 and *mi*6 samples. A summary of the analysis is shown in Table 1. All the sample EDS spectra generally confirm (Fig. 1) the presence of calcium, iron, silicon, aluminum and magnesium; however, some minor differences are observed among the samples that allow the division into two groups.

3.1.1. First group

This group is constituted by *mi*1, *mi*2 and *mi*3 samples. The EDS spectra and FTIR analysis of this group of samples show that the pigment is constituted by yellow iron oxides.

Thus, for example, in Fig. 2 the infrared spectrum of *mi*1 is shown. We can identify calcite (bands at 2515, 1439, 874 and 705 cm^{-1}), common clayey silicates like illite (band at 1027 cm^{-1} with a shoulder at 1092 cm^{-1}) and yellow iron oxides (bands at 912 and 799 cm^{-1}). This last compound is considered the pigment that defines the sample color. Some of the band shapes are due to the sum of more than one vibrational band of the aforementioned compounds (i.e. the wide band sited at 3425 cm^{-1} with a shoulder to 3180 cm^{-1}).

These results are corroborated by XRD. The presence of goethite is detected according to the attribution made from the FTIR spectrum.

3.1.2. Second group

This group is constituted by *mi*4, *mi*5 and *mi*6 samples. By XRD technique apart from calcite, quartz and some silicates, the presence of iron oxides in the form of goethite, cuprorivaite (Egyptian blue) and cinnabar (HgS) has been detected (Fig. 3). Because of the coincidence of cuprorivaite, XRD data with an artificial calcium copper silicate, the so-called Egyptian blue pigment, the accepted formula for the last one pigment is the cuprorivaite formula ($CaCuSi_4O_{10}$). Studies by IR, UV and VIS spectroscopies about this pigment are very scarce and, by this reason, we decided to synthesize the pigment using the Ullrich [11] recipe. The compound obtained has been posi-

Table 1
General characteristics of the ocher and reddish samples studied

Group	Sample	Chromatic composition			$\lambda_{dominant}$ (nm)	Saturation (%)	Chemical composition	
		x_{10}	y_{10}	Y_{10}			Pigment	Base
Ocher colors	*mi*1	0.3929	0.3768	46.645	579.0	35.9	Goethite	$CaCO_3$
	*mi*2	0.3765	0.3616	29.352	581.5	26.3	Goethite	$CaCO_3$
	*mi*3	0.3675	0.3637	35.691	579.0	25.0	Goethite	$CaCO_3$
	*mi*4	0.3935	0.3698	18.699	581.5	37.5	Goethite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*5	0.4093	0.3734	22.545	582.5	27.2	Goethite, cinnabar, Egyptian blue	$CaCO_3$
	*mi*6	0.3976	0.3873	21.513	577.0	39.5	Goethite, Egyptian blue, cinnabar	$CaCO_3$
Reddish colors	*mi*7	0.3598	0.3362	12.459	600.0	14.3	Cinnabar, hematite	$CaCO_3$
	*mi*8	0.4149	0.3520	23.199	593.0	34.8	Cinnabar, hematite	$CaCO_3$
	*mi*9	0.4098	0.3471	11.874	595.0	31.9	Cinnabar, hematite	$CaCO_3$
	*mi*10	0.4125	0.3416	15.373	600.0	30.6	Cinnabar, hematite	$CaCO_3$
	*mi*11	0.4170	0.3422	13.176	600.0	33.7	Cinnabar, hematite	$CaCO_3$
	*mi*12	0.3885	0.3392	17.153	600.0	23.5	Cinnabar, hematite	$CaCO_3$
	*mi*13	0.3793	0.3511	21.289	587.0	24.4	Hematite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*14	0.3545	0.3436	14.559	587.0	15.1	Hematite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*15	0.3427	0.3386	18.647	590.0	10.2	Hematite, cinnabar, Egyptian blue	$CaCO_3$
	*mi*16	0.3786	0.3577	11.796	584.0	25.6	Hematite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*17	0.3905	0.3624	32.658	584.0	30.5	Hematite, goethite, cinnabar	$CaCO_3$
	*mi*18	0.3527	0.3552	15.513	578.0	18.4	Hematite, Egyptian blue	$CaCO_3$

The main compounds of the pigmentary layer and binder are shown. The chromatic coordinates, luminosity, dominant wavelength and saturation of each sample are exposed.

tively identified as cuprorivaite by XRD. The FTIR, UV and VIS spectra of the synthesized pigment have been used to corroborate its presence in the samples [1].

In Fig. 4, the infrared spectrum of *mi*5 sample is shown as an example; the bands associated with the presence of calcite, illite and yellow iron oxides are detected. On the other hand, the band appearing at 1027 cm^{-1} that presents a shoulder at 1092 cm^{-1} attributed to the presence of illite modifies its shape due to the presence of Egyptian blue (bands at 1160, 1079, 1054 and 1009 cm^{-1}). It is

Table 2
General characteristics of the bluish and greenish studied

Group	Sample	Chromatic composition			$\lambda_{dominant}$ (nm)	Saturation	Chemical composition	
		x_{10}	y_{10}	Y_{10}			Pigment	Base
Bluish colors	*mi*19	0.2858	0.3204	48.287	480.5	12.5	Egyptian blue	$CaCO_3$
	*mi*20	0.2925	0.3221	35.844	480.0	10.0	Egyptian blue	$CaCO_3$
Greenish colors	*mi*21	0.3527	0.3744	33.861	569.5	23.0	Green earth	$CaCO_3$
	*mi*22	0.3575	0.3776	20.977	570.0	25.7	Green earth	$CaCO_3$
	*mi*23	0.3572	0.3765	22.314	570.0	25.7	Green earth	$CaCO_3$
	*mi*24	0.3633	0.3801	23.168	571.0	28.4	Green earth	$CaCO_3$
	*mi*25	0.3451	0.3608	27.174	571.5	17.6	Malachite	$CaCO_3$
	*mi*26	0.3227	0.3611	21.138	557.0	10.0	Egyptian blue, goethite	$CaCO_3$

The main compounds of the pigmentary layer and binder are shown. The chromatic coordinates, luminosity, dominant wavelength and saturation of each sample are exposed.

Table 3
General characteristics of the white, gray and black samples studied

Group	Sample	Chromatic composition			$\lambda_{\text{dominant}}$ (nm)	Saturation (%)	Chemical composition	
		x_{10}	y_{10}	Y_{10}			Pigment	Base
White colors	*mi*27	0.3612	0.3625	43.229	577.0	22.4	Calcite, dolomite, goethite, cinnabar	$CaCO_3$
	*mi*28	0.3667	0.3662	60.005	577.0	25.0	Calcite, dolomite, goethite, cinnabar	$CaCO_3$
	*mi*29	0.3640	0.3639	55.379	577.0	23.7	Calcite, dolomite, goethite, cinnabar	$CaCO_3$
	*mi*30	0.3557	0.3612	50.408	575.0	21.0	Calcite, dolomite, goethite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*31	0.3530	0.3598	40.101	575.0	21.0	Calcite, dolomite, goethite, Egyptian blue, cinnabar	$CaCO_3$
	*mi*32	0.3452	0.3531	50.881	576.0	15.8	Calcite, dolomite, Egyptian blue	$CaCO_3$
	*mi*33	0.3641	0.3685	47.884	575.0	26.3	Calcite, dolomite, goethite, cinnabar	$CaCO_3$
Gray colors	*mi*34	0.3117	0.3363	30.181	–	–	Egyptian blue, iron oxides	$CaCO_3$
	*mi*35	0.3196	0.3406	26.618	–	–	Egyptian blue, iron oxides	$CaCO_3$
Black colors	*mi*36	0.3180	0.3331	14.792	–	–	Graphite	$CaCO_3$
	*mi*37	0.3115	0.3279	14.109	–	–	Graphite	$CaCO_3$
	*mi*38	0.3203	0.3343	14.250	–	–	Graphite	$CaCO_3$
	*mi*39	0.3176	0.3302	7.818	–	–	Graphite	$CaCO_3$
	*mi*40	0.3208	0.3327	8.541	–	–	Graphite	$CaCO_3$

The main compounds of the pigmentary layer and binder are shown. The chromatic coordinates, luminosity, dominant wavelength and saturation of each sample are exposed.

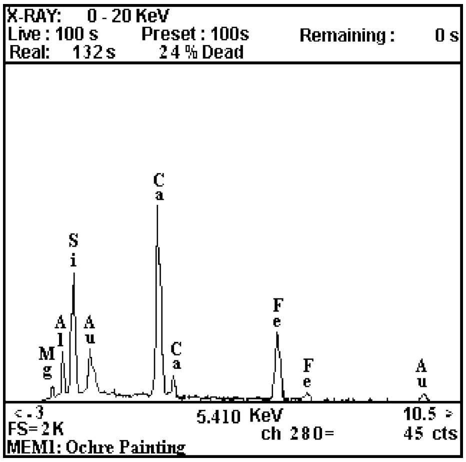


Fig. 1. EDS spectrum of an ocher painting sample where the presence of calcium, silicon, aluminum, magnesium and iron is observed. The last element can be associated to the presence of iron oxides.

not possible to observe any band due to cinnabar in the conventional working range of this technique.

From EDS, besides the aforementioned elements, the presence of chemical elements constituting the Egyptian blue and cinnabar are observed. Egyptian blue crystals are more abundant in the *mi*6 sample. Cinnabar is detected as tiny points being more abundant in the *mi*5 sample.

In this group of six samples (Table 1, Fig. 5), the chromatic characterization indicates that they present a medium saturation, a high pigment concentration, with a dominant wavelength around 580 nm. However, the variation in wavelength of the samples containing Egyptian blue and cinnabar (*mi*4, *mi*5 and *mi*6) is justified by variations in the proportions of these two minority components. Thus, the *mi*4 sample presents the same value as *mi*2 that only has presented goethite. On the one hand, if the proportion of

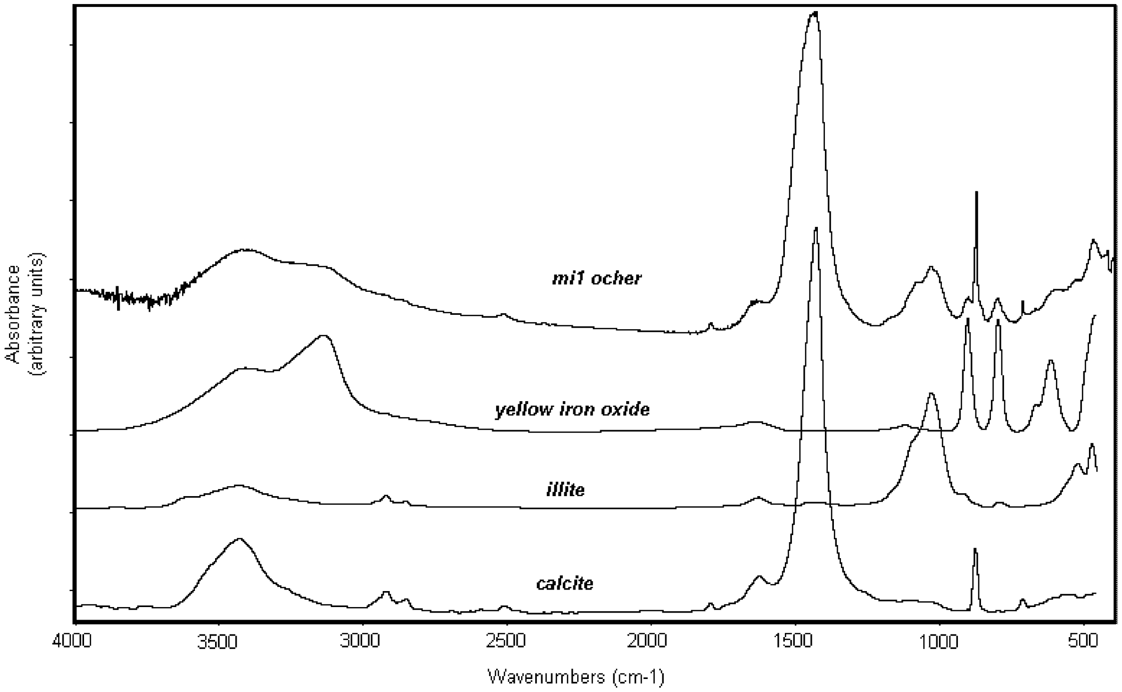


Fig. 2. FTIR spectrum of the *mi*1 ocher sample. Besides the typical substances of the binder, it is possible to detect yellow iron oxide as pigment of the pictorial surface.

Egyptian blue increases, a reduction of the aforementioned wavelength to the greenish-yellow zone is observed. This is the case of the *mi*6 sample, the predominant wavelength presents the lowest value

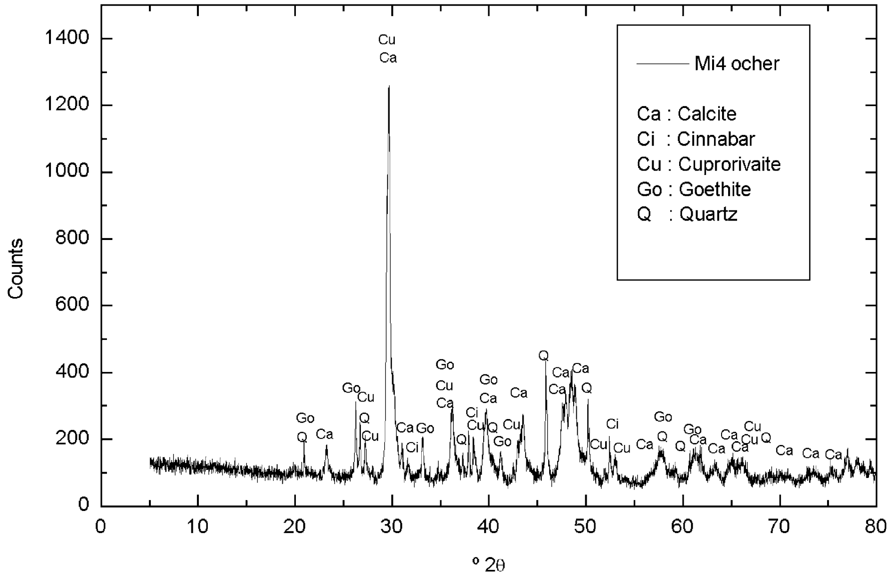


Fig. 3. X-ray diffractogram of the *mi*4 ocher sample. Goethite, cuprorivaite, cinnabar, calcite and quartz are detected.

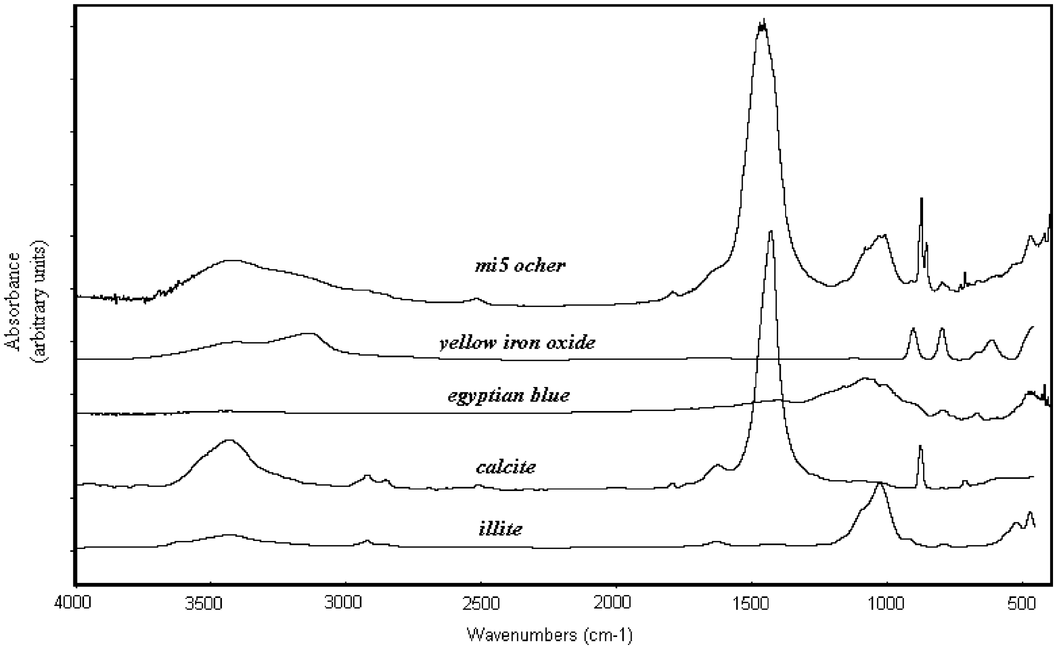


Fig. 4. FTIR spectrum of the *mi*5 ocher sample. Besides the typical substances of the binder, it is possible to detect yellow iron oxide and Egyptian blue as pigments of the pictorial surface.

in the group ($\lambda_{\text{dominant}} = 577$ nm). On the other hand, if the proportion of Egyptian blue decreases and the proportion of cinnabar increases, a rise of the dominant wavelength to the reddish-yellow zone is observed. The sample that presents the highest wavelength is *mi*5 ($\lambda_{\text{dominant}} = 582.5$ nm).

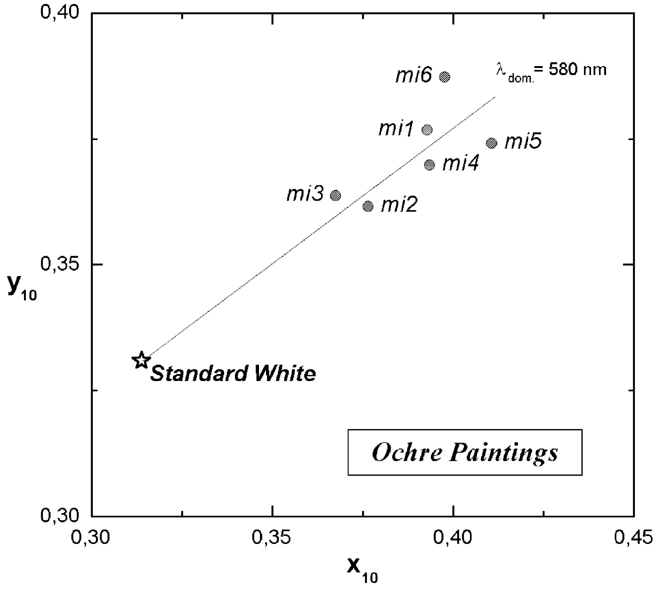


Fig. 5. CIE64 chromatic diagram enlargement for the ocher samples.

Every sample presents a medium or a low luminosity that may be caused by the substrate on that the pigment is painted. Every sample is on a black-painted base except for the *mi*1 sample that is painted over *mi*2. It may be emphasized that the lower luminosity values are observed in the samples with Egyptian blue.

3.2. Reddish colors

This color is highly variable and the description as "reddish" sometimes depends on the interpretation of the observer. The distinction between the shades of red and the derivatives of red is usually due to the mixture of red with white, black, yellow, blue or green.

The results obtained for these samples are summarized in Table 1. The chromatic results shown in this table indicate that every sample has a medium or a low luminosity. Furthermore, it may be observed that the dominant wavelength of the samples (Table 1, Fig. 6) allows to put them into these groups: (a) vermilion reds, with the highest wavelength between 600 and 593 nm, (b) ocher reds, with a dominant wavelength between 590 and 584 nm, and a low luminosity, (c) pink, with a dominant wavelength of 584 nm and a medium luminosity and (d) brown, with a wavelength of 578 nm and low luminosity.

3.2.1. Vermilion reds

Formed by the *mi*7, *mi*8, *mi*9, *mi*10, *mi*11 and *mi*12 samples. The EDS spectra of these samples confirm the presence of sulfur and mercury, constituent elements of cinnabar, with iron in lower proportion in addition to calcium and silicon (Fig. 7a). Using scanning electron microscopy (SEM) in backscattering mode, it is observed that the cinnabar layer is covered with a very thin layer of iron oxides, as a protector film or patina. This could explain why this color has not blackened if it is exposed to light (Fig. 7b).

In diffractograms, as well as quartz, calcite, dolomite and several silicates, the presence of cinnabar as a basic constituent of this pigment and the presence of iron oxides in the shape of hematite to a greater or lesser extent are detected. In Fig. 8, the diffractogram corresponding to the *mi*11 sample is shown as an example. The presence of cinnabar as the main component in the pigment and a little amount of hematite has been detected. The FTIR spectra confirm the presence of the aforementioned substances.

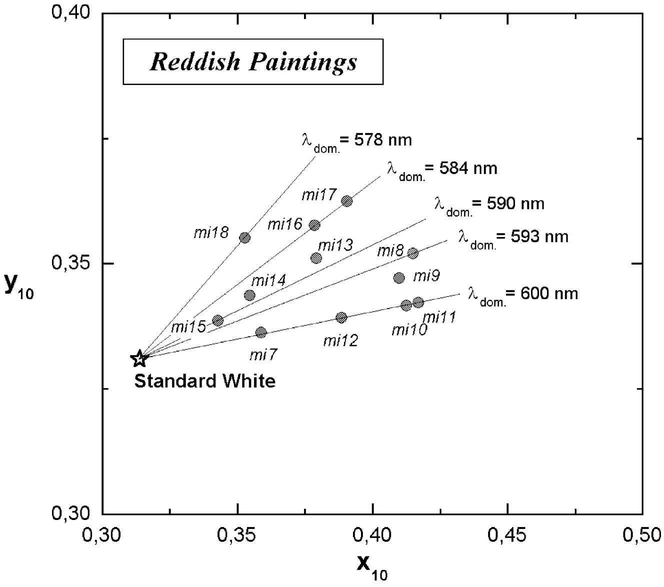
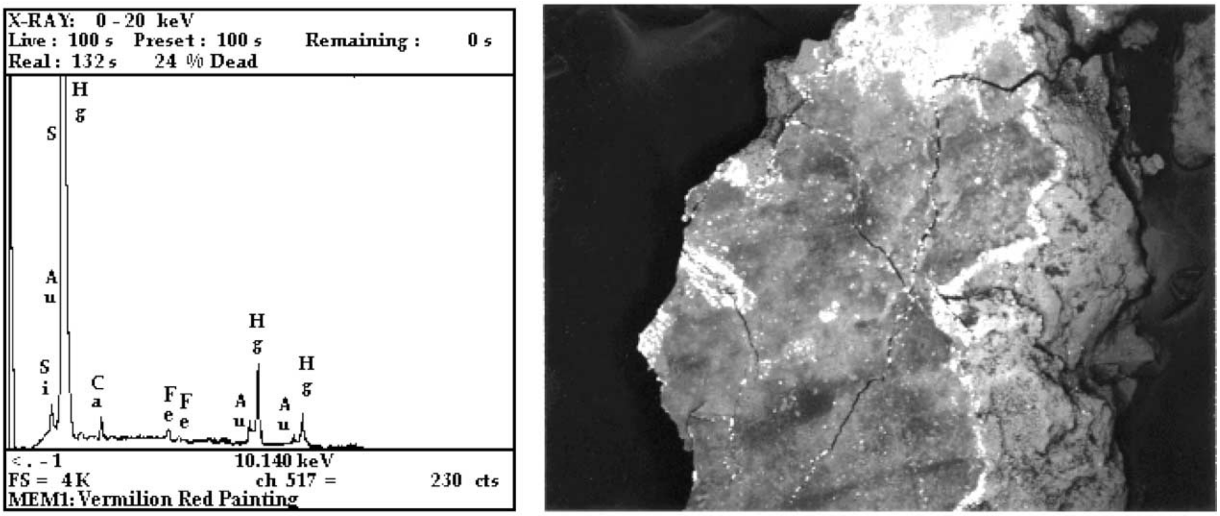


Fig. 6. CIE64 chromatic diagram enlargement for the reddish samples.



(a)

(b)

Fig. 7. (a) EDS spectrum of a vermilion red painting sample where the presence of mercury and sulfur, associated to the presence of cinnabar is observed; (b) backscattering image of *mi*8 sample. It is observed that the cinnabar layer is covered by a very thin covering of iron oxides, as a protector film or patina.

3.2.2. *Ocher reds*

Formed by *mi*13, *mi*14, *mi*15 and *mi*16 samples. The EDS spectra of the samples confirm the presence of silicon, iron and calcium in great amounts that indicate the presence of iron oxides as the main component of the pigment, and in some sporadic places the constituent elements of cinnabar or Egyptian blue are found.

These substances are confirmed by XRD; in these samples besides quartz, calcite and several

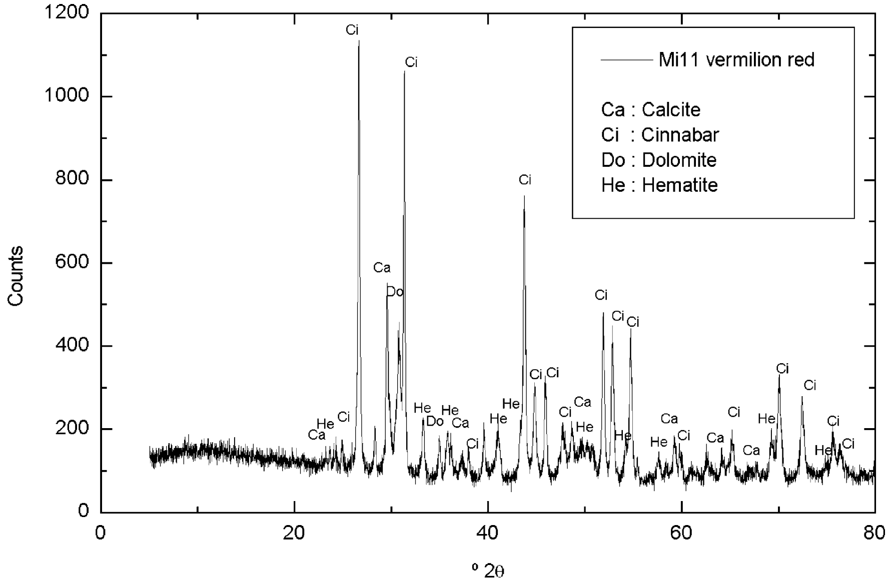


Fig. 8. XRD of the *mi*11 vermilion red sample. Cinnabar, hematite, calcite and dolomite are detected.

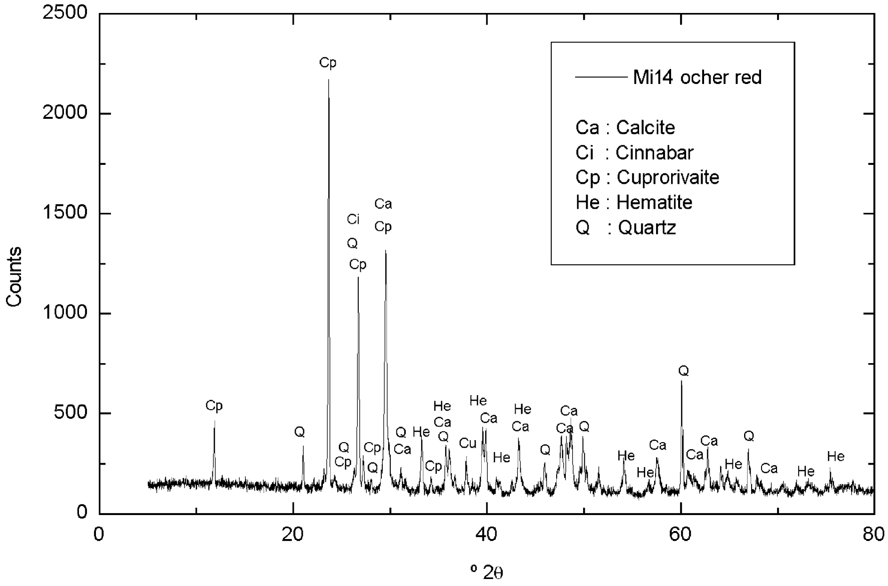


Fig. 9. XRD of the *mi*14 ocher red sample. Hematite, cinnabar, cuprorivaite, calcite and quartz are detected.

silicates, the presence of hematite is detected as the basic constituent of this pigment. In the samples, the presence of little amounts of cinnabar and Egyptian blue is also observed. In Fig. 9, the *mi*14 sample diffractogram is shown in that the presence of all these aforementioned substances is observed.

On the other hand, the FTIR spectra confirm the presence of substances using all other techniques. Thus, in Fig. 10, the infrared spectrum of one sample of the *mi*16 is shown. Underneath this spectrum, the calcium carbonate and iron oxides spectra (bands at 1081, 795, 642 and 534 cm^{-1}) appear. The bands located at 1160, 1079, 1054 and 1009 cm^{-1} may be ascribed to the presence of Egyptian blue, observing how the band at 1054 cm^{-1} increases its intensity because the contribution of the band appearing at 1050 cm^{-1} attributed to the presence of illite. Other spectral bands owe its form to the sum of different contributions; thus, for example, the wide band at 3425 cm^{-1} is due to the sum of the bands of the three aforementioned compounds.

3.2.3. *Pink*

It is constituted by the *mi*17 sample. Its EDS spectrum confirms the presence of the constituent elements of the iron oxides as the main components of the pigment, and the constituent elements of cinnabar in some dispersed points. Its diffractogram indicates, besides the existence of quartz, calcite and several silicates, the presence of hematite and goethite as basic constituents of this pigment. Also, a large amount of calcium carbonate and magnesium (dolomite) and little amounts of cinnabar are observed.

3.2.4. *Brown*

Made up only of *mi*18 sample. An enormous amount of blue crystals appears on a reddish-ocher background in the microscopic observation. The EDS spectrum of this sample confirms the presence of calcium, silicon and iron, as well as the constituent elements of Egyptian blue as main components of the pigment and some amount of cinnabar in localized regions, that may be ascribed to the contamination of the paintbrush.

In the corresponding diffractogram, besides quartz, calcite and dolomite, and several silicates, the presence of hematite and Egyptian blue as basic constituents of this pigment are detected (Fig. 11).

Comparing the chromatic characterization with different subgroups chemical compositions (Table 1, Fig. 6), it is observed that if the content in iron

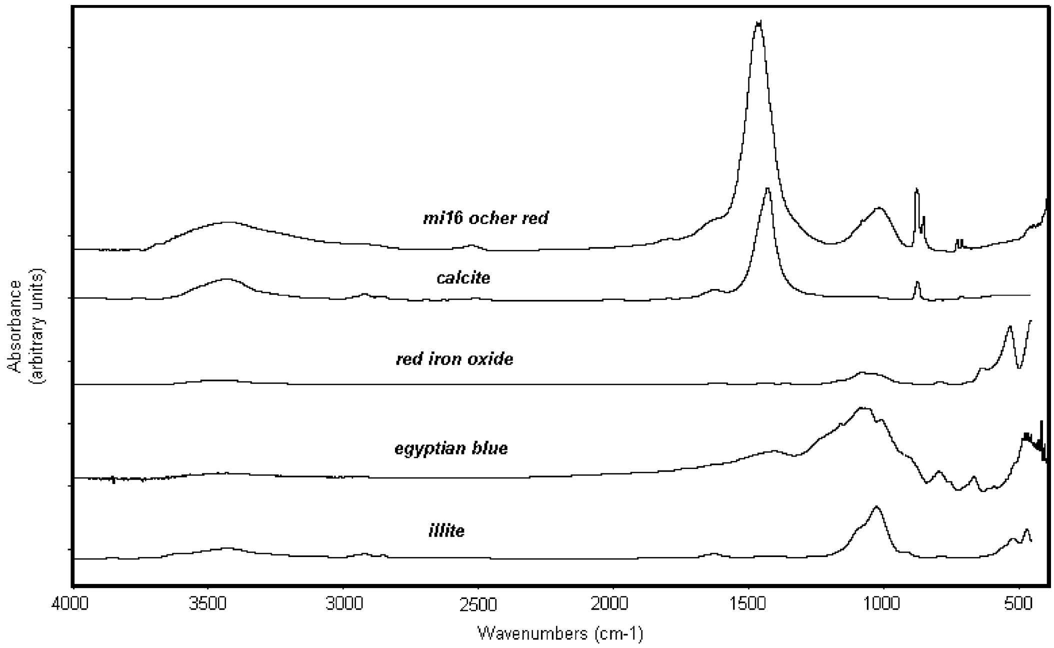


Fig. 10. FTIR spectrum of the *mi*16 ocher red sample. Red iron oxide and Egyptian blue as pigment and a mixture of calcite and common silicates as illite as binder can be detected.

oxides in relation to cinnabar and Egyptian blue increases, the wavelength will decrease to the ocher red samples group zone and the pink sample, where the presence of iron oxides (and not cinnabar) is majority, obtaining wavelengths between 590 and 584 nm. The significantly lower

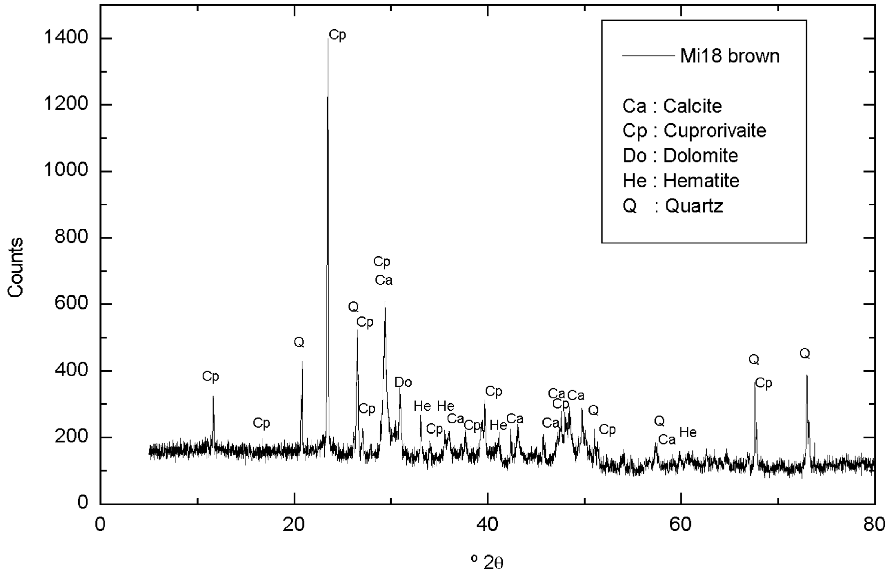


Fig. 11. X-ray diffractogram of the *mi*18 brown sample. Hematite, cuprorivaite, dolomite, calcite and quartz are detected.

dominant wavelength in the *mi*18 sample is due to the great amount of Egyptian blue.

3.3. Bluish colors

This color appears in the *mi*19 and *mi*20 samples. The experimental results are shown in Table 2. The chromatic coordinates are aligned in the CIE64 diagram (Fig. 12), with a low saturation and a dominant wavelength value around 480.2 nm. This seems to indicate that the samples present the same kind of pigment.

The EDS spectra confirm the presence of silicon, calcium and copper. The existence of these elements is an indication of the presence of Egyptian blue. By means of XRD, besides silicon oxide in the crystallographic variety of quartz, calcium carbonate in the crystallographic variety of calcite and several silicates, the presence of cuprorivaite as a basic constituent of this pigment is detected. In Fig. 13, the diffractogram of the *mi*20 sample is shown as an example.

In the same way, the FTIR infrared spectra of these blue samples adjust to the substance yet found in the previous techniques and no bands are observed that may indicate the presence of organic substances. Thus, in Fig. 14, the infrared spectrum of the *mi*19 sample is shown. Underneath this spectrum, calcium carbonate, common silicates (as illite) and Egyptian blue spectra are shown.

3.4. Greenish colors

This color appears in the *mi*21, *mi*22, *mi*23, *mi*24, *mi*25 and *mi*26 samples. The chromatic characterization (Table 2, Fig. 15) shows substantial differences that let us classify the samples in three groups.

3.4.1. First group

It is composed by *mi*21, *mi*22, *mi*23 and *mi*24 samples that show a dominant wavelength around 570 nm (Table 2), corresponding to the yellowish-green zone. The EDS spectrum of the samples confirms the presence of calcium and the constituent elements of the aluminum, potassium and iron silicates (Fig. 16a). This seems to indicate the presence of green earth as pigment in these samples. The pigment called "green earth" [10,12–16] is the most frequent form of green

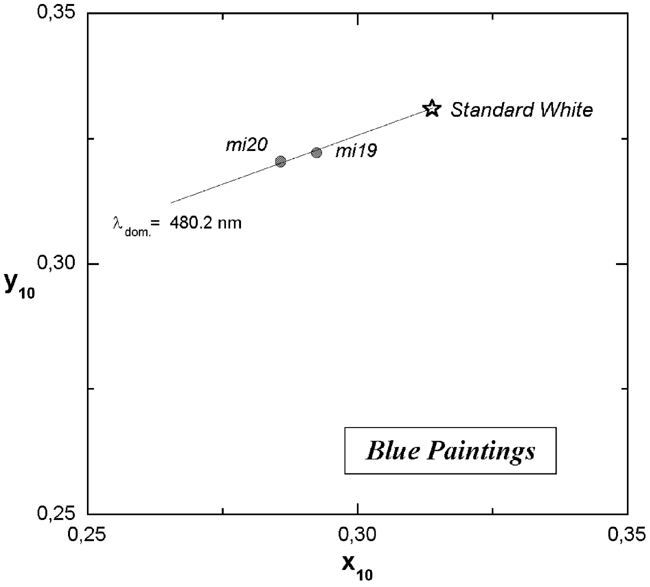


Fig. 12. CIE64 chromatic diagram enlargement for the blue samples.

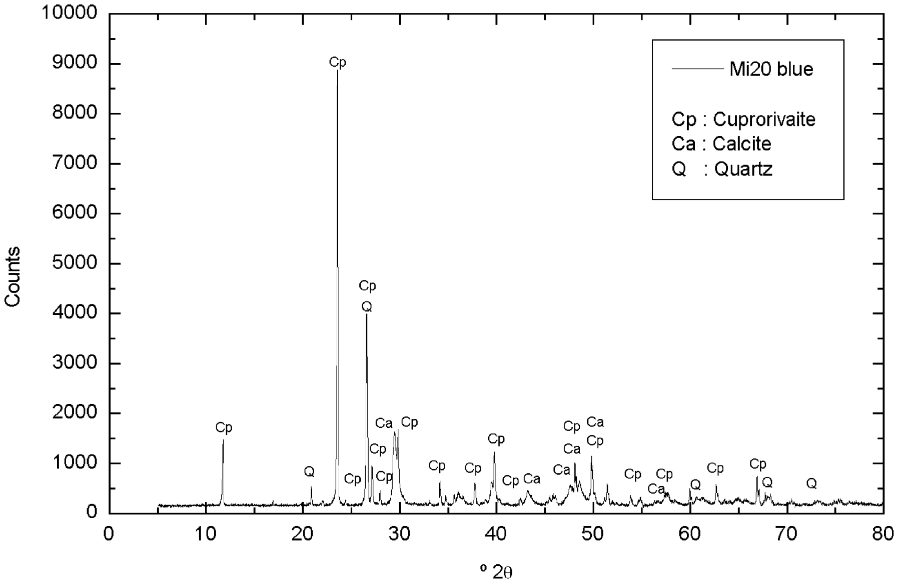


Fig. 13. X-ray diffractogram of the *mi*20 blue sample. Cuprorivaite, calcite and quartz are detected.

color in Roman wall paintings. According to Delamare [12], a mixture of clays is embraced under the name of green earth and the most important of them are glauconite, celadonite and the chlorite group (clinochlore and penninite); all of these are aluminum silicates with impurities of

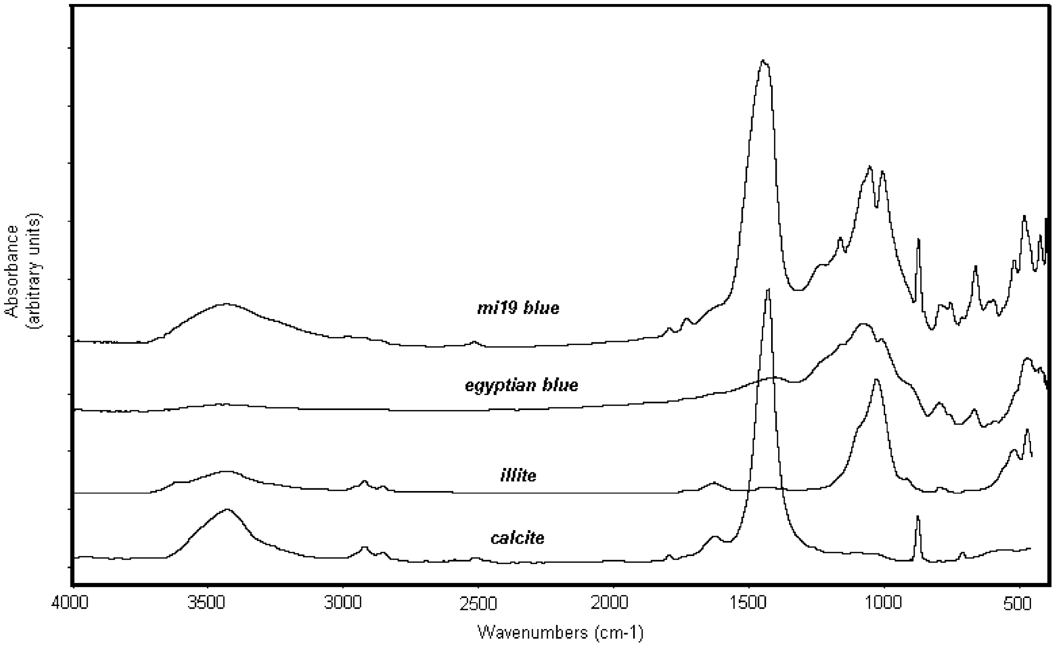


Fig. 14. FTIR spectrum of the *mi*19 blue sample. The pigmentary substance is Egyptian blue. The binder compounds are a mixture of calcite and common silicates as illite.

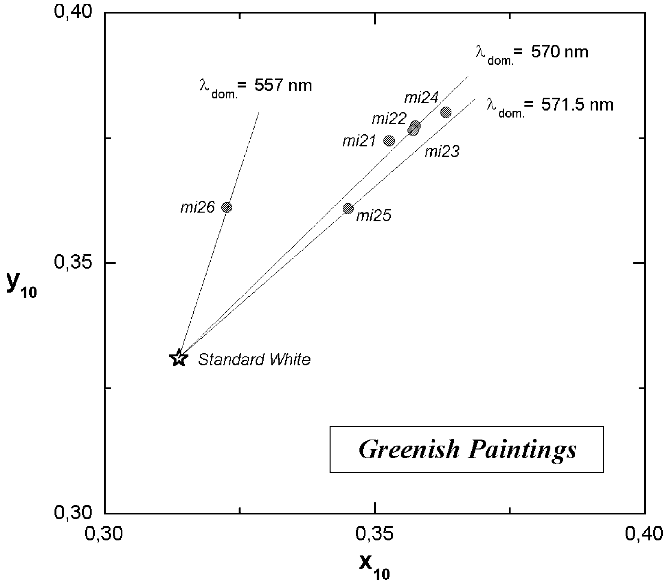


Fig. 15. CIE64 chromatic diagram enlargement for the greenish samples.

Fe^{2+}, Fe^{3+}, K^{+} and other ions. The crystal shape of these silicates is observed using SEM (Fig. 16b).

The XRD confirms the presence of this pigment; thus, in Fig. 17 the *mi*21 sample diffractogram is shown, where, besides quartz, calcite, dolomite and several silicates, the presence of clinochlore as a basic constituent of this pigment is found. As we aforementioned, this compound is included among the possible substances that may compose a part of those known as green earth.

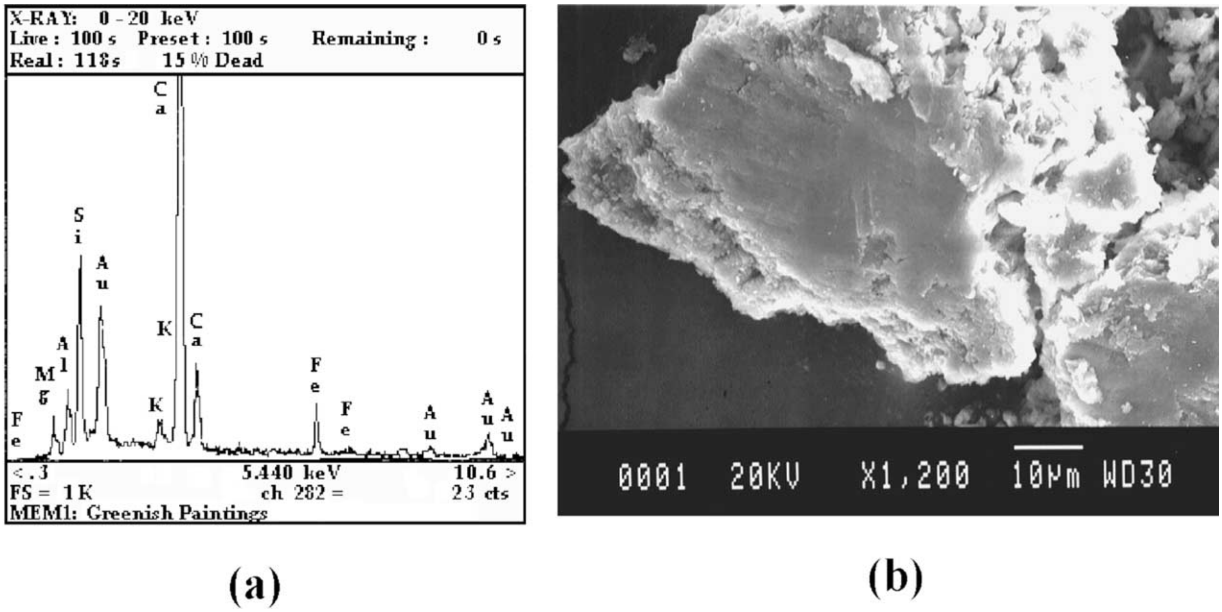


Fig. 16. (a) EDS spectrum of the *mi*22 green painting sample. The detection of magnesium, aluminum, silicon, potassium and iron can be associated with the presence of green earths; (b) SEM image of green earth crystals observed in *mi*22 green painting sample.

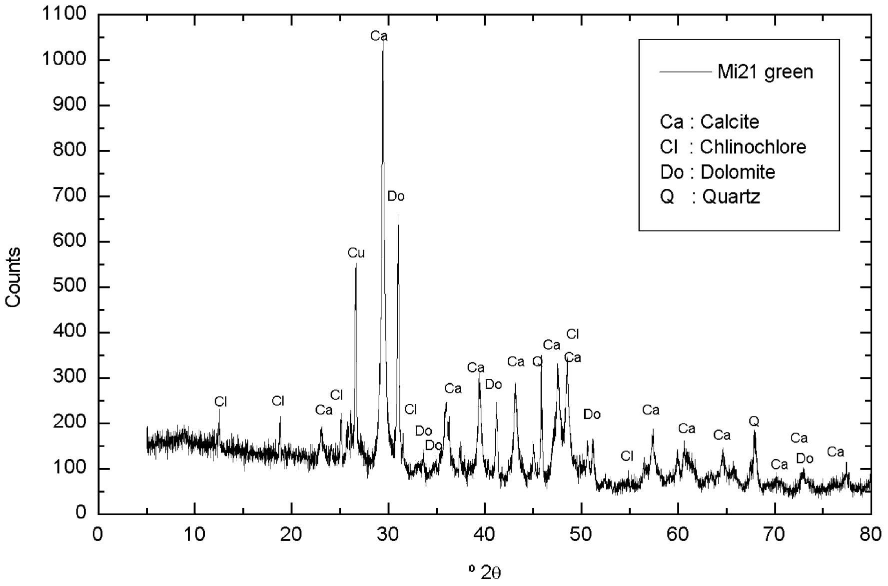


Fig. 17. XRD of the *mi*21 green sample. Clinochlore, calcite, dolomite and quartz are detected.

3.4.2. Second group

It is formed by the *mi*25 sample. It shows a higher wavelength, 571.5 nm (Table 2) with a lower saturation compared to the first group samples. The EDS spectrum of this sample (Fig. 18a) confirms the presence, besides the calcium

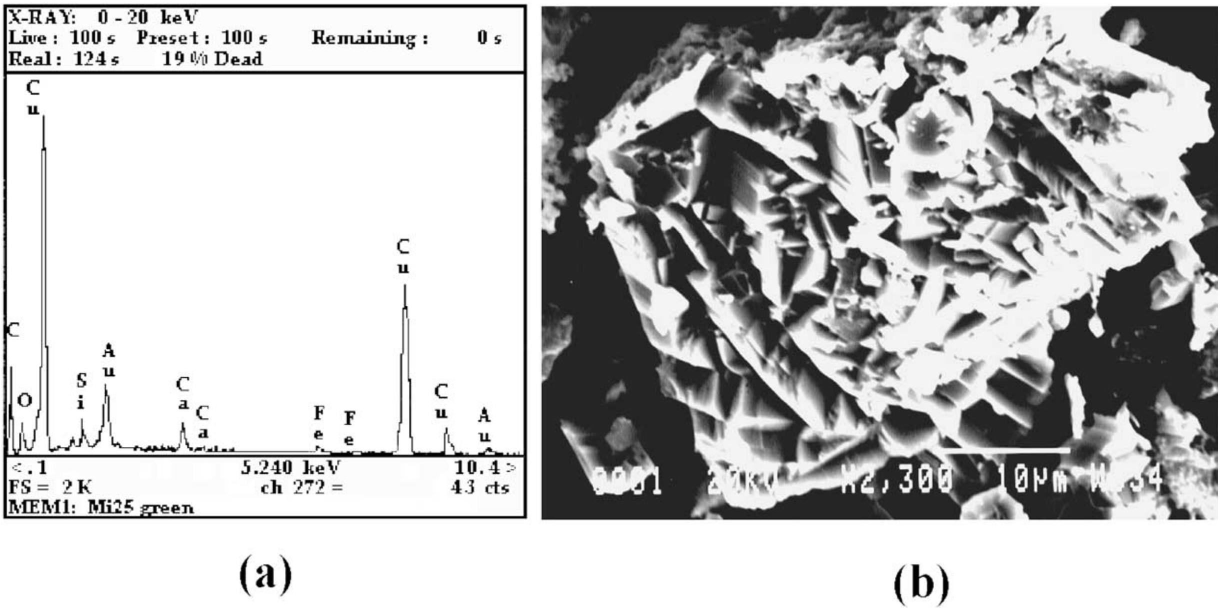


Fig. 18. (a) EDS spectrum of the *mi*25 green painting sample. The detection of copper, oxygen and carbon can be associated with the presence of malachite; (b) SEM image of malachite crystals observed in *mi*25 green painting sample.

and common silicate elements, the corresponding elements to copper carbonates, that may indicate that the pigment could be azurite or malachite. Using SEM, the form of these crystals is observed appearing as an aggregate of prismatic crystals (Fig. 18b).

The XRD investigation confirms, besides quartz, calcite, dolomite and several silicates, the presence of malachite as constituent of the pigment (Fig. 19). On the other hand, its infrared spectrum (Fig. 20) shows a band series that are justified because the presence of the compounds that were found with other techniques. Malachite band assignation has been made by comparison with those shown in the work of Gettens and Fitzhugh [17]. Thus, for example, the bands at 1483, 820, 758, 578 and 522 cm^{-1} may be ascribed to the presence of malachite and the bands at 1422, 874 and 712 cm^{-1} are the result of the sum of the contributions of calcium carbonate and malachite bands. In the same way, the bands at 1096 and 1047 cm^{-1} may be attributed to the sum of contributions of common silicates and malachite bands. Other bands of the spectrum owe their forms to the sum of more than one vibrational band of the aforementioned compounds (i.e. the wide band between 3500 and 3300 cm^{-1} with two peaks at 3405 and 3314 cm^{-1}).

3.4.3. Third group

Formed by the *mi*26 sample that presents a dominant wavelength (557 nm) lower than other samples and a lower luminosity. Thus, the tonality of this sample is green compared with other samples that present a yellowish-green tonality. The X-ray diffractogram of this sample (Fig. 21) indicates the presence of cuprorivaite and yellow iron oxides mainly in the form of goethite. In the FTIR spectrum, the bands associated with the presence of calcite, Egyptian blue and yellow iron oxides are detected.

These results indicate that the green color in the *mi*26 sample is not due to the use of green pigments as green earth or malachite but is obtained from the Egyptian blue and yellow iron oxides (goethite) mixture.

3.5. White colors

This appears in *mi*27, *mi*28, *mi*29, *mi*30, *mi*31, *mi*32 and *mi*33 samples. The EDS spectra show the presence of calcium, silicon, aluminum and

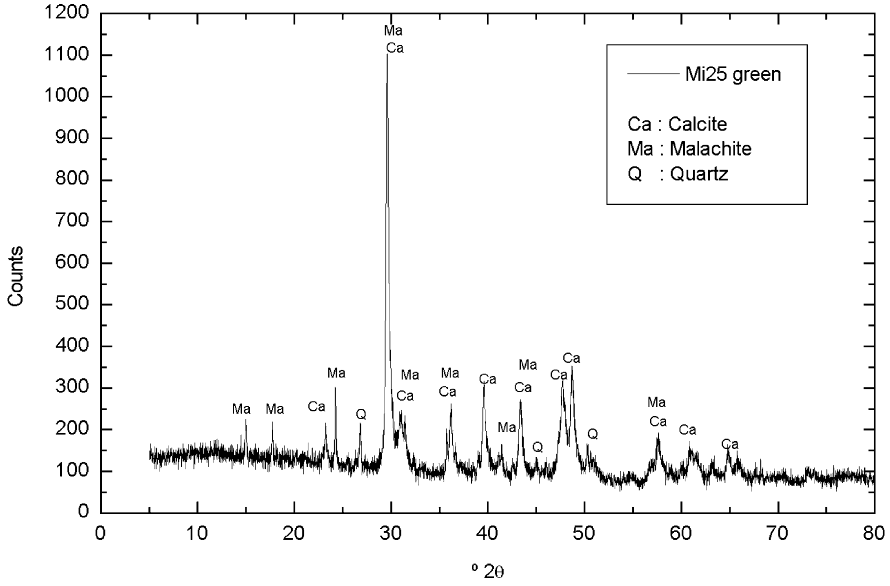


Fig. 19. XRD of the *mi*25 green sample. Malachite, calcite and quartz are detected.

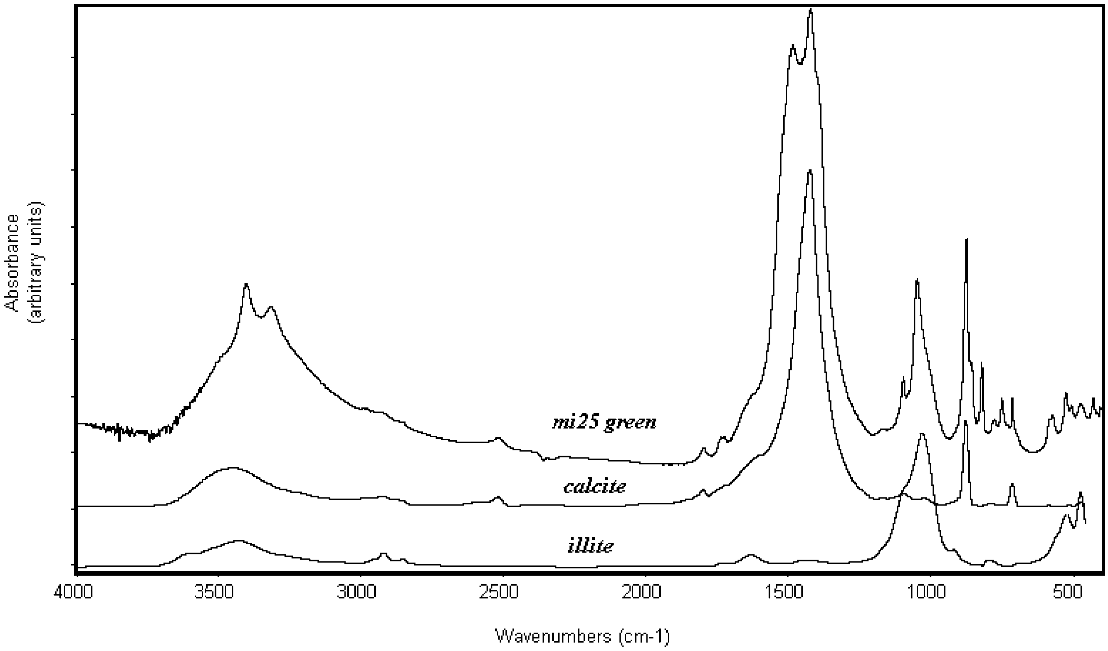


Fig. 20. FTIR spectrum of the *mi*25 green sample. Malachite bands assignation has been made by comparison with those shown in the works of Gettens et al.

magnesium in a higher proportion than the corresponding to a common silicate, a low amount of iron and the cinnabar constituents (Hg and S).

In *mi*30, *mi*31 and *mi*32 samples, the chemical constituent elements of Egyptian Blue were also detected in certain points (Fig. 22).

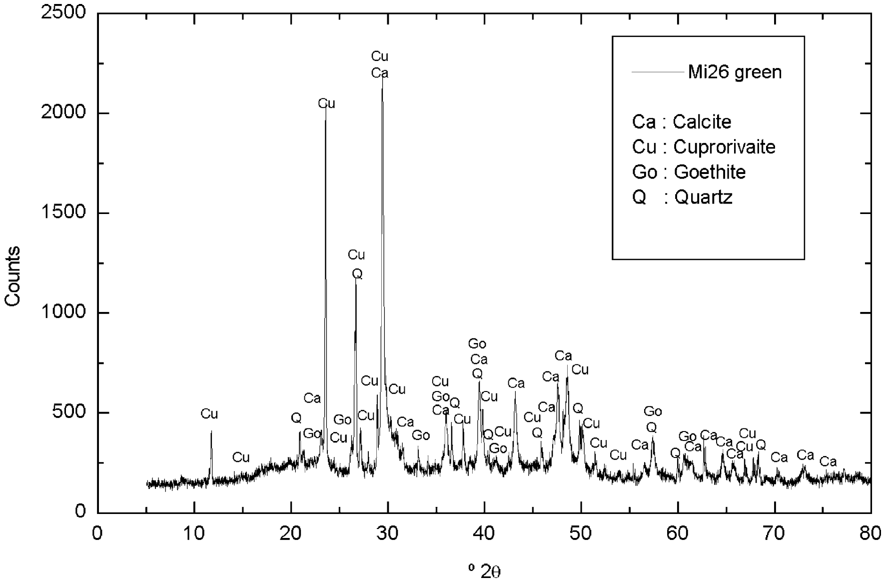


Fig. 21. XRD of the *mi*26 green sample. Goethite, cuprorivaite, calcite and quartz are detected.

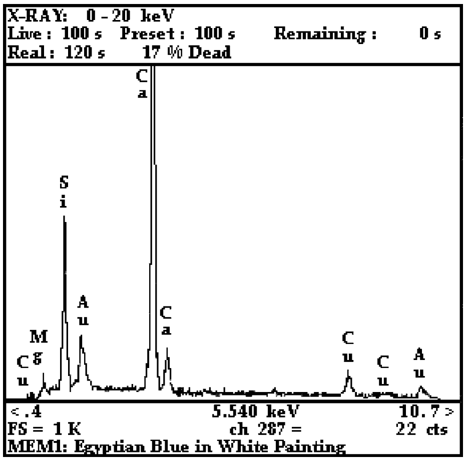


Fig. 22. EDS spectrum of blue crystal of the *mi*31 white painting sample. The detection of copper, calcium and silicon can be associated with the presence of Egyptian blue and, magnesium and calcium with carbonates.

These substances are confirmed using XRD and FTIR. Thus, in Fig. 23 the diffractogram of the *mi*31 sample is shown. Besides quartz and several silicates, the presence of dolomite and calcite as basic constituents of this pigment and the shorter presence of goethite, cinnabar and Egyptian blue is observed. All the bands of the infrared spectra of the samples are justified with the aforementioned compound bands.

In the chromatic characterization (Table 3, Fig. 24), all samples present a dominant wavelength between 575 and 577 nm. These wavelength values indicate that they are actually situated in the yellowish zone but the saturation and luminosity values provoke a yellowish-white visual sensation.

The addition of Egyptian blue to the white pigment (*mi*31, *mi*32 and *mi*33) provokes a decrease of the saturation in the color (having a lower luminosity) compared with other white samples, being more pronounced in the case of *mi*32 (15.8%). This is the reason why this sample is the one found in the nearest point to the white, having a medium luminosity. We suppose that this addition of Egyptian blue has been carried out to reinforce the white coloration.

3.6. Gray colors

The *mi*34 and *mi*35 samples form this group. These samples have very low saturation values and

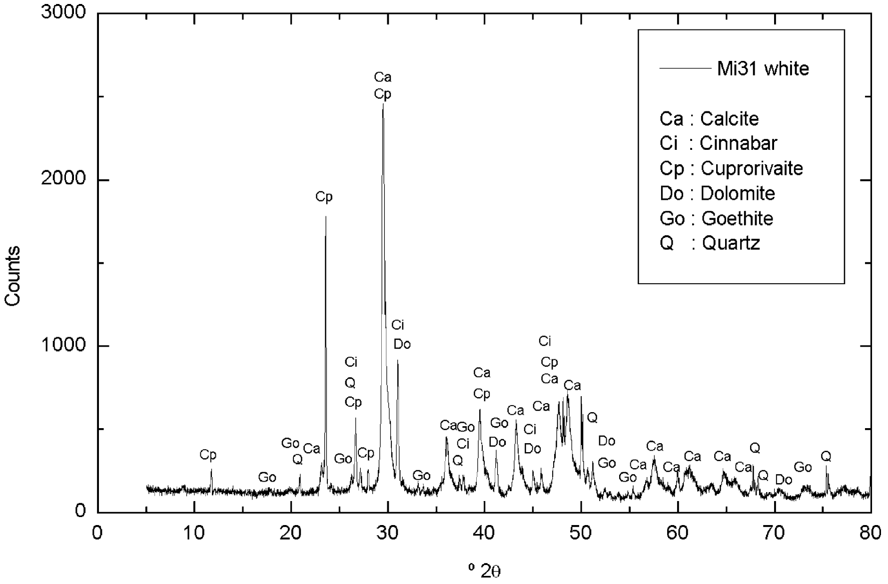


Fig. 23. XRD of the *mi*31 white sample. Calcite, dolomite, cinnabar, cuprorivaite, goethite and quartz are detected.

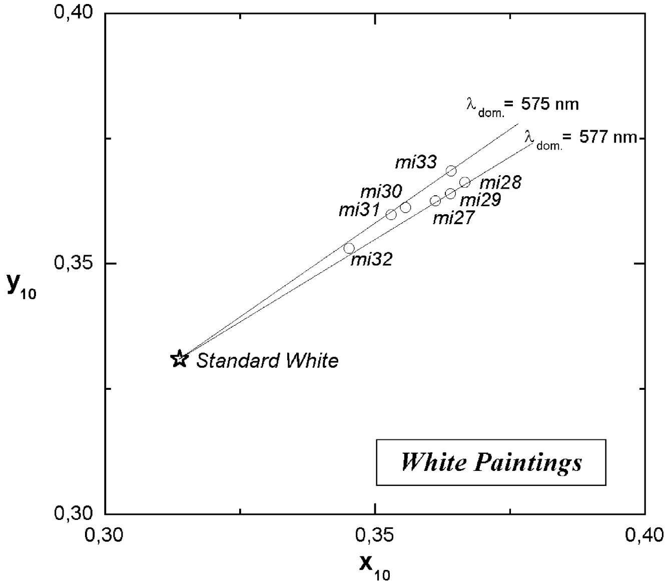


Fig. 24. CIE64 chromatic diagram enlargement for the white samples.

medium luminosity (Table 3, Fig. 25a), i.e. they provide an achromatic stimulus corresponding to the visual interpretation of grays. This low saturation is possible to get with two different methods:

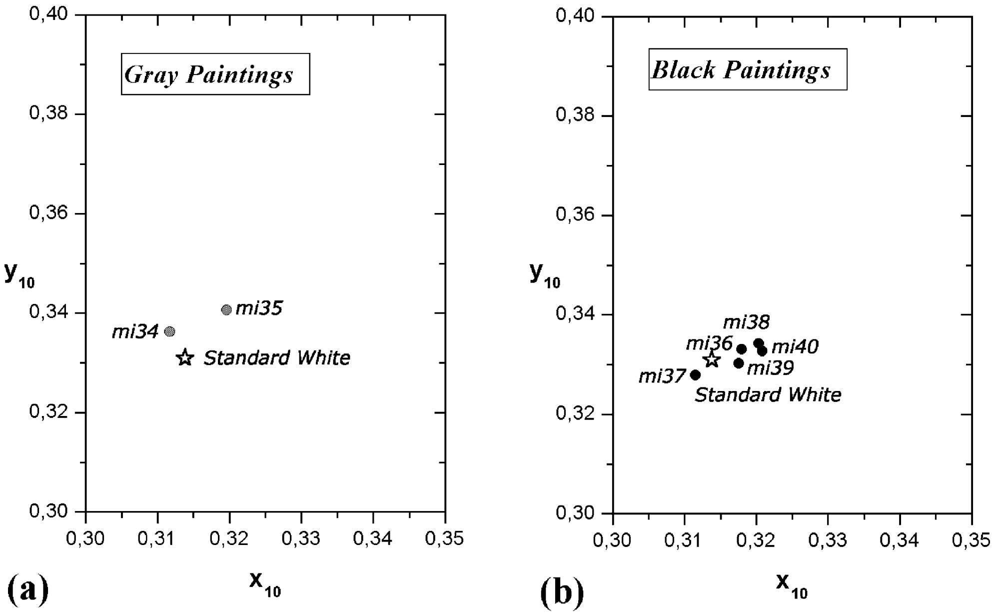


Fig. 25. (a) CIE64 chromatic diagram enlargement for the gray samples; (b) CIE64 chromatic diagram enlargement for the black samples.

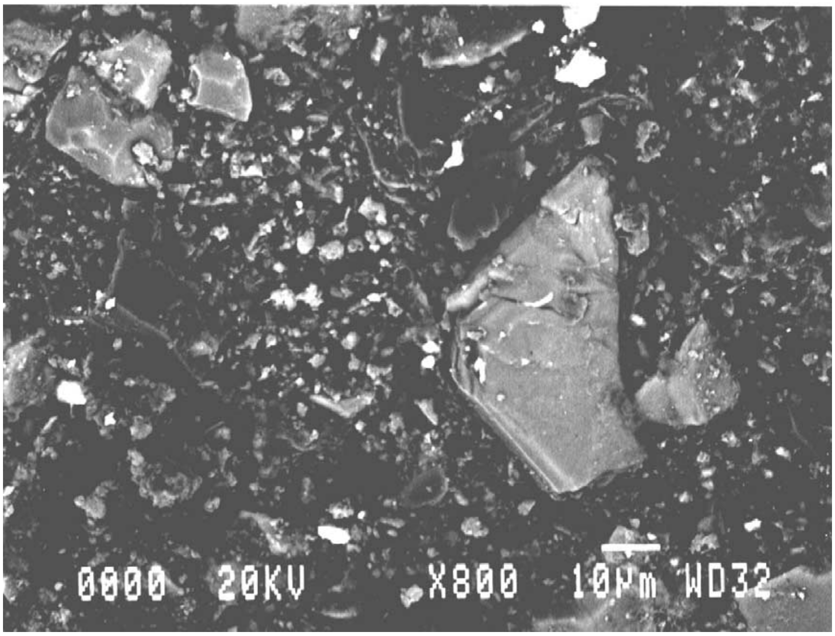


Fig. 26. Backscattering image of Egyptian blue crystals observed in *mi*35 gray painting sample.

(a) by a low pigment concentration in a white binder or (b) adding any pigment that desaturates the color of the majority pigment [7,8].

The gray color samples are a clear example of the second method. The use of an optical microscope shows blue crystals over an ocher background. The EDS spectra confirm the presence of silicon, calcium, copper, and little amounts of iron. The presence of the first three elements is an indication of the existence of Egyptian blue (as the majority pigment) and the fourth is of the iron oxides. Some Egyptian blue crystals in the sample *mi*35 are shown in Fig. 26 using electron microscopy as a backscattering technique.

All these compounds are detected using XRD techniques, where iron oxide appears as maghemite-C or as hematite form.

3.7. Black colors

The black color appears in the *mi*36, *mi*37, *mi*38, *mi*39 and *mi*40 samples. The chromatic characterization (Table 3, Fig. 25b) shows that all the samples are grouped around the achromatic point and present a low or very low luminosity that characterizes this achromatic stimulus.

The XRD study reveals the presence of calcite, common silicates; a little amount of carbon in the form of graphite, as well as iron oxides although in low amounts and in the magnetite forms (Fig. 27).

In order to confirm the presence of magnetite, each one of the sample was treated with 1 N hydrochloric acid to eliminate the presence of carbonates, and the EDS spectrum was made. In all cases, the presence of iron and oxygen (Fig. 28) was observed.

The presence of little amounts of magnetite seems to indicate a mineral origin of the carbon that was used. However, we assume that the amount of this pigment is too small to generate all the black color. Then the existence of another carbon morphology as amorphous carbon is feasible.

4. Conclusions

To accomplish the compositional analysis of Roman wall paintings, the most convenient

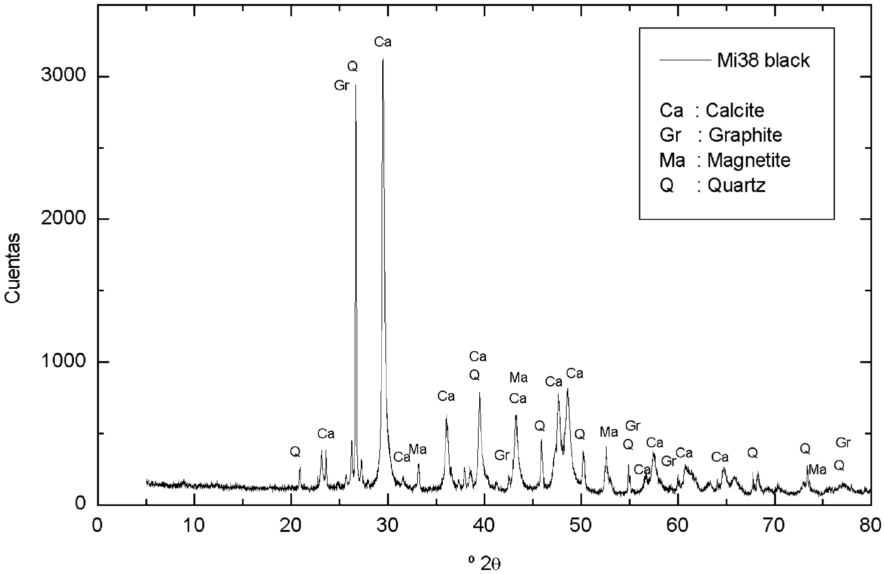
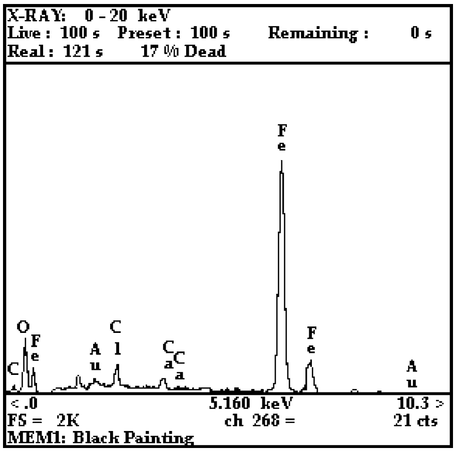


Fig. 27. X-ray diffractogram of the *mi*38 black sample. Graphite, magnetite, calcite and quartz are detected.

method is to group the samples by chromatic criteria. The most suitable way to determine the chromatic characteristic of a sample is to use the reflectance spectroscopy in the visible region and then to apply a normalized process of chromatic coordinate calculus defined by CIE64. The ulterior atomic and molecular analysis, by spectroscopic techniques such as EDS and FTIR, and the crystallographic analysis by diffractometric methods such as XRD, applied to each chromatic group allow a correct identification of pigments as well as the pictorial techniques that we have been used.



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X-RAY:  0 - 20 keV
Live : 100 s   Preset : 100 s      Remaining :      0 s
Real : 121 s     17 % Dead
< .0                        5.160 keV             10.3 >
FS =  2K                    ch  268 =             21 cts
MEM1: Black Painting
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Fig. 28. EDS spectrum of a black painting sample, previously treated with 1 N hydrochloric acid. It is observed the presence of iron and oxygen. The peak corresponding to chlorine is due to the treatment received by this sample.

The application of the aforementioned techniques has allowed to ensure that the mural paintings studied from Casa del Mitreo have high quality because in all cases, the pigment is supported in lime mortar (calcium carbonate) and it has not been found any plaster in the mortar, not even as base of the pictorial surface as in other samples [1]. Regarding to the pictorial technique used, no sign that indicates the presence of organic substances like wax and soap have been found. It allows deducing that the called “fresco painting” technique has been used for applying the colors.

Regarding to the different color types that appear in the samples, we can deduce the following conclusions:

- The use of some catalogued pigments in the literature as of high cost and of great quality (e.g. cinnabar, malachite, Egyptian blue, etc.)

makes us suppose that this house belonged to a high social class or high purchasing power.

- It has been found some pigment mixtures barely described in the bibliography and even in some cases they are new.
- The ocher colors have been obtained mainly by the yellow iron oxides in the shape of goethite. In some cases, low amounts of Egyptian blue or cinnabar have been added in order to modify its tonality. This Egyptian blue and cinnabar addition to the ocher colors is not described in the bibliography.
- The reds and their derivates are obtained by mixtures in different proportions of cinnabar and red iron oxides, which have permitted the division of the samples in four groups:
  - Vermilion reds present a great amount of cinnabar. The use of this pigment is not usual in Roman paintings due to its high cost, being 16 times more expensive than ocher reds. Vitruvio comments [14] that some paintings with this pigment blackened due to its exposure to light. The incorporation of iron oxides that in these samples appear as a protector film may justify the non-blackening in these paintings.
  - Ocher reds have a majority concentration of iron oxides, presenting some of them little amounts of cinnabar or Egyptian blue.
  - The pink sample has been obtained by a mixture of iron oxides with calcite and dolomite and a little amount of cinnabar.
  - The brown sample has been obtained by red iron oxides and Egyptian blue mixture. This way to obtain this tonality is unusual.
- The blue colors have been obtained exclusively by Egyptian blue.
- The green colors have been obtained by three different ways:
  - By means of green earth that is the most frequent way to obtain the green coloration in the Roman wall paintings.
  - Using malachite, rarely used in Roman wall paintings due to its high cost.
  - By means of the mixture of Egyptian blue and yellow iron oxides. This mixture of pigments to obtain a green coloration is not described in the bibliography.
- The white colors are mainly obtained from dolomite and calcite, observing in some of them the addition of Egyptian blue to increase the sensation of white. In the consulted bibliography, this kind of mixture does not appear.
- The gray colors are obtained from the decreasing saturation of Egyptian blue with little amounts of red iron oxides.
- The black colors seem to be carbon from mineral origin due to the presence of iron oxides.

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