

ANALYSIS OF EARTH PIGMENTS IN PALOMINO'S FRESCOES IN THE SANTOS JUANES CHURCH IN VALENCIA (SPAIN) BY SOLID STATE VOLTAMMETRY AND FTIR SPECTROSCOPY

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ABSTRACT: *A combination of solid-state voltammetry and Fourier transform infrared spectroscopy in the attenuated total reflectance mode was applied to identify earth pigments in samples from the frescoes of Antonio Palomino (dated 1707) taken from the vault of the Santos Juanes church in Valencia (Spain). Such frescoes suffered considerable damage by fire during the Spanish Civil War in 1936, resulting in severe chemical and chromatic alterations.*

KEYWORDS: solid state voltammetry, FTIR spectroscopy, iron oxide pigments, earth pigments, Santos Juanes church, Antonio Palomino, wall painting

INTRODUCTION

Identification of pigments used in paint layers can be considered as one of the most relevant analytical targets during the scientific examination of works of art (Feller, 1986; Roy, 1993; Fitzhugh, 1997). Other than the need to take minimal amounts of samples, this aim is made difficult by the multi-component nature of paint layers, in which different pigments can be accompanied by binders and other materials. This problem increases notably in instances where paintings have suffered severe damage. This is the case of the frescoes of Acisclo Palomino, painted in 1707 in the vault of the Santos Juanes church in Valencia (Spain). These frescoes suffered considerable deterioration by fire during the Spanish Civil War in 1936, resulting in chromatic alterations. This problem is particularly relevant for a family of temperature-sensitive pigments, earths or iron earths, which are extensively used by Palomino in his paintings.

Earths can be considered as a family of iron pigments which, on the basis of their mineralogy, can be divided into clayey earths, calcium sulphate-based earths, umbers and iron silicates. Clayey earths are mainly composed by Al-substituted goethite (FeO(OH)), kaolinite and quartz, resulting from the lateritic weathering of mafic rocks. Hematite (α -Fe₂O₃) can substitute goethite as the main iron component, such as that found in Red bole. Gypsum-type earths are probably evaporitic materials where goethite (yellow earths) or hematite (red earths) are accompanied by gypsum, anhydrite and clay minerals. Dark earths are goethite-based pigments that are probably originated by the weathering of iron minerals such as iron sulphides, and eventually accompanied by manganese oxides. Green earths are formed by iron silicates (mainly glauconite and celadonite), which in turn are accompanied by clays and manganese oxide. Some pigments are manufactured materials; thus, Venetian red is a synthetic mixture of hematite and dolomite produced traditionally by the calcination of carbonates and ferrous sulphate.

Earths are, therefore, multi-component materials where iron oxides with a variable degree of crystallinity and hydration are accompanied by kaolinite, quartz, gypsum, anhydrite, calcite, and other minerals. The hue of the pigments varies from pale yellow (when goethite is the main iron oxide) to dark red (when hematite dominates) to brown or a greenish hue. The colour of earths is due to the absorption associated with the charge transfer between the ligand (OH⁻ and O²⁻) and the Fe³⁺ ion contained in goethite and/or hematite, and depends significantly on the shape and size of the particles distribution (Elias et al., 2006). The greenish hue of green earths is attributable to glauconite and celadonite.

The most common techniques for identifying earth pigments are scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM/EDX) (Elias et al., 2006), X-ray diffraction (XRD) (Mazzocchin et al., 2004; Colombini et al., 2004; Grygar et al., 2003; Edreira et al., 2003), Fourier transform infrared spectroscopy (FTIR) (Mazzocchin et al., 2004; Colombini et al., 2004; Grygar et al., 2003; Edreira et al., 2003), Raman spectroscopy (Bell et al., 1997; David et al., 2001), X-ray photoelectron spectroscopy (XPS) ((De Benedetto et al., 1998; Sabbatini et al., 2000), X-ray fluorescence (XRF) (Bell et al., 1997), and solid-state voltammetry (Doménech et al., 2001; Grygar et al., 2002).

In this work, we report a procedure for the identification of earths based on a combination of attenuated total reflectance/Fourier transform infrared spectroscopy (ATR/FTIR) and voltammetry of microparticles (VMP), a modality of solid-state electrochemistry. This last-mentioned methodology has recently claimed considerable attention (Scholz and Meyer, 1998; Grygar et al., 2000). Chemometric methods, which use data provided by the aforementioned techniques, are applied for identifying earth pigments, which in our case, are original earth pigments in samples taken from Palomino's frescoes in the Santos Juanes church.

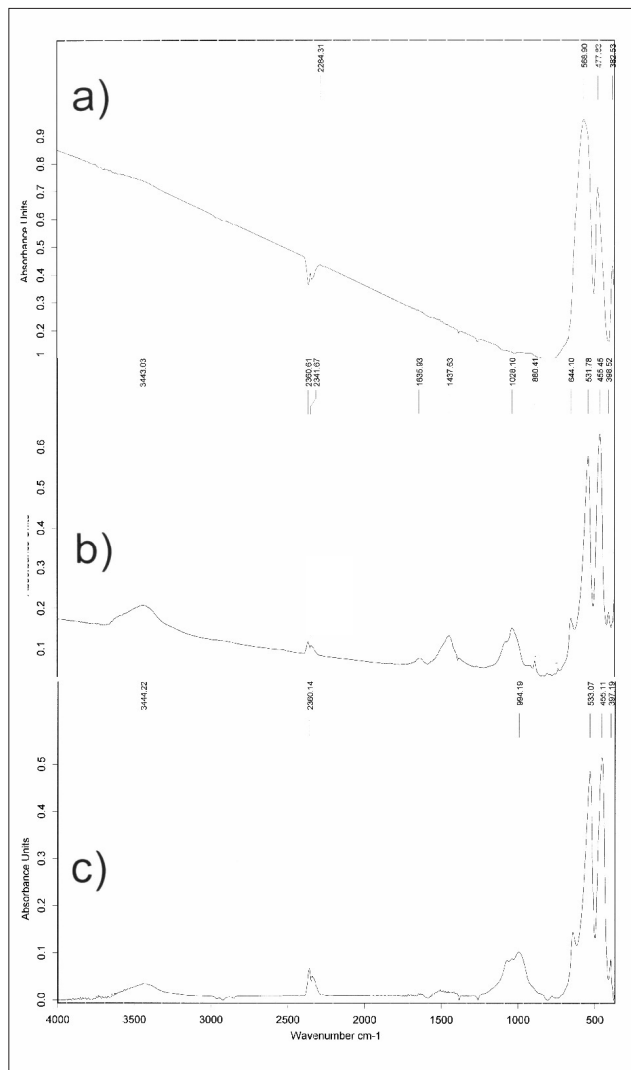


Figure 1. IR absorption spectra of: a) hematite; b) pristine Spanish hematite; c) Spanish hematite heated at 600 °C for 24 h.

EXPERIMENTAL

Spanish hematite, Caput mortum, Venetian red, Orange French ochre, Yellow French ochre, Red clay, Red bole, Spanish ochre, Sienna raw, Natural Sienna, Cyprus umber, and Italian umber, all supported by Kremer, were used as reference pigments. Fe_2O_3 (Aldrich) was taken as hematite reference material. Four samples, labelled as TR3a, TR3b, TR4a, TR4b, were studied. The samples were taken with a sharp tip of a microscalpel and placed on a concavity slide. Then the paint layers were mechanically separated by using a scalpel with diamond lancets, a diamond dissecting knife and tungsten needles with the help of a stereoscopic light microscope with a wide separation between the stage and the objective lens. The sample was further grounded and homogenised in a small agate mortar and transferred to the PIGE surface. The same procedure as used for pigment blanks was followed. PIGEs consisted of 5 mm diameter cylindrical rods prepared as described in the literature (Scholz and Meyer, 1998). The blanks of pigments and the samples were accurately powdered in an agate mortar and pestle. The powdered sample (5-10 mg) was placed on a glazed porcelain tile, forming a spot of finely distributed material. Then the lower end of the graphite electrode was gently rubbed over that spot of sample and finally cleaned with a tissue paper.

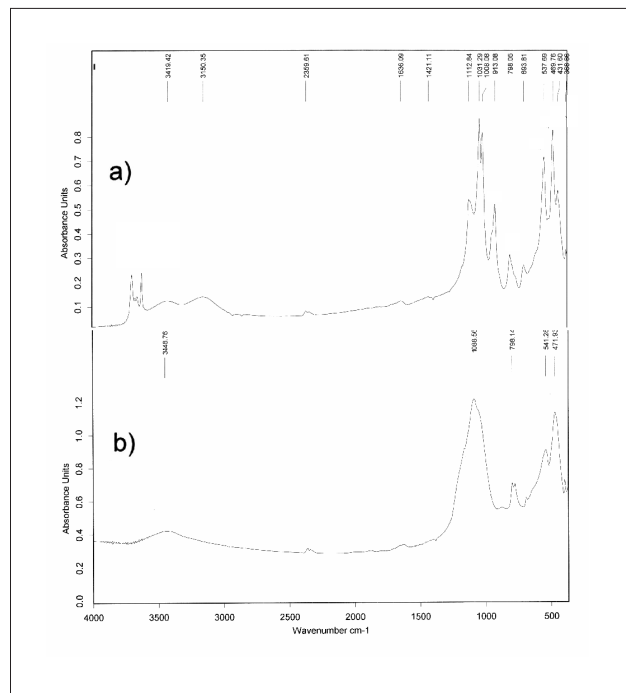


Figure 2. IR absorption spectra of: a) pristine French ochre; b) French ochre heated at 600 °C for 24 h.

All electrochemical experiments were performed at 298 K after the immersion of the modified electrodes in deaerated solutions using the CH I420 equipment. A conventional three-electrode arrangement was used with a PIGE working electrode, a Pt-wire auxiliary electrode and an AgCl (3 M NaCl)/Ag reference electrode. Cyclic and square wave voltammetries were used. Eventually, the convolution of voltammetric curves was performed in order to improve peak resolution.

IR absorption spectra were performed in the attenuated total reflectance mode (ATR) with a Vertex 70 Fourier transform infrared spectrometer and with a FR-DGTS (fast recovery deuterated triglycine sulphate) temperature-stabilised coated detector. The number of co-added scans was 32; resolution: 4 cm^{-1} .

RESULTS AND DISCUSSION

FTIR Spectroscopy of iron oxide pigments

IR absorption spectrum of iron(III) oxide consists of two prominent, characteristic bands at 470 and 540 cm^{-1} , as can be seen in Fig. 1a corresponding to hematite. Similarly, Fig. 1b shows the IR absorption spectrum of Spanish hematite where prominent bands at 530 and 455 cm^{-1} are also found. Moreover, bands centred at 3443 and 1635 cm^{-1} correspond to hydrohematite, while the weak peak at 880 and 795 cm^{-1} denotes the presence of a small amount of goethite. Sharp stretching bands in the region from 1000 to 1100 cm^{-1} are attributable to kaolin group minerals, while a band at 1437 cm^{-1} must be attributed to carbonates, as typically observed in ceramic materials. Figure 1c presents the IR absorption spectrum of a Spanish hematite sample submitted to heating at 600 °C for 24 h. Bands at 3444 cm^{-1} decrease significantly while goethite peaks at 880 and 795 cm^{-1} and carbonate peaks at 1437 cm^{-1} disappear entirely.

These assignments are in agreement with the literature data. Thus, Yariv and Mendelovici (1979) reported that the IR spectrum of a well crystallised hematite differs drastically from that of poor crystalline protohematite. Grinding slightly affects the spectra of both

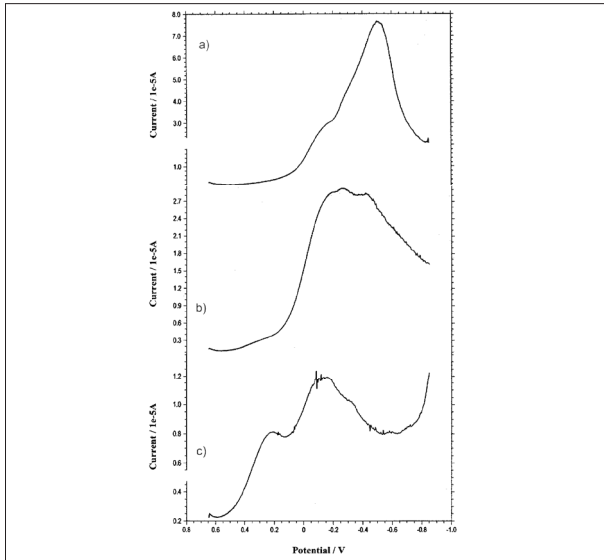


Figure 3. SQWVs of PIGEs modified with: a) Spanish hematite, b) Orange French ochre, c) Italian umber, immersed into 0.10 M HCl. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

Modifier	I(II)	I(III)	I(IV)
Spanish hematite	0.06	0.32	0.60
Spanish hematite*	0.23	0.28	0.87
Caput mortuum	0.02	0.27	0.43
Venetian red	0.05	0.22	0.40
Orange French ochre	0.23	0.39	1.00
Orange French ochre*	0.42	0.30	0.87
Yellow French ochre	0.10	0.36	1.00
Yellow French ochre*	0.15	0.22	0.83
Red clay	0.34	1.00	0.70
Red bole	0.16	1.00	0.73
Spanish ochre	0.12	0.78	1.00
Sienna raw	0.15	1.00	0.85
Natural Sienna	0.05	1.00	0.98
Cyprus umber	0.40	1.00	0.46
Italian umber	0.83	1.00	0.70
Italian umber*	1.00	0.32	0.87
TR3a	0.04	0.18	0.43
TR4b	0.02	0.10	0.38
TR5b	0.06	0.18	1.00
TR6a	0.10	0.22	0.80

Table 1. Normalized peak current data for pristine pigments. From SQWVs of sample-modified PIGEs immersed into 0.10 M HCl. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. Samples submitted to thermal treatment at 600 °C during 24 h are noted by *

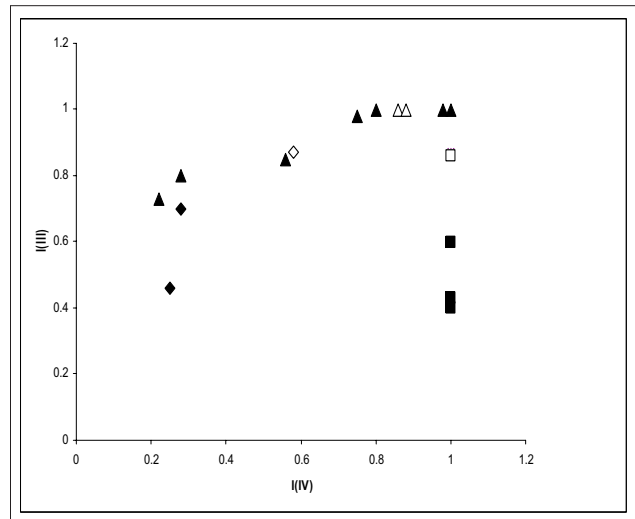


Figure 4. Two-dimensional diagram for earths. Plots of I(III) vs. I(IV) for hematite-based pigments (solid squares), ochres (solid triangles) and umbers (solid rhombs). Data for pigments heated at 600 °C corresponding to Spanish hematite (square), French ochres (triangles) and Natural umber (rhomb) are shown.

protohematite and hematite. Dehydroxylation of goethite occurs at 250°C, leading to the protohematite and recrystallisation of protohematite, giving a hematite at 430°C, but not in powdered samples. Goethite exhibits bands at 3212-3194, 1687-1674, 1643-1640, 888-884, 800-798, 3450-3445 622-617 and 461-459 cm⁻¹. Hydrohematite shows characteristic bands at 950 and 630 cm⁻¹ whereas maghemite presents IR absorption bands at 724, 694, 638, 584, 558, 442 and 396 cm⁻¹ (Veintimillas-Verdaguer et al., 1998; Belin et al., 2002). Heating a hematite in oxygen brought about two effects, a reversible surface dehydroxylation and an irreversible sintering of the hematite particles. At 500°C, hematite gives a transitional oxide leading maghemite, which was partly transformed into magnetite at 600°C.

Ruan et al. (2001) studied the behaviour of the hydroxyl units of synthetic goethite and its dehydroxylated product hematite. Five intense OH vibrations at 3212-3194, 1687-1674, 1643-1640, 888-884 and 800-798 cm⁻¹, and a water vibration at 3450-3445 cm⁻¹, were observed for goethite. Bands at 622-617 and 461-459 cm⁻¹ were also detected at the low-frequency region. IR absorption spectrum of goethite exhibits an intense band at 3450-3445 cm⁻¹ attributed to the hydroxyl stretching. This band decreased only slightly during the decomposition of goethite and, conjointly with the band at 1630 cm⁻¹ which was attributed to a so-called 'loosely bound water', is indicative of an excess of hydroxyl units in hematite, which corresponds to hydrohematite. The bands near 3400, 950 and 630 cm⁻¹ were reported as being hydroxyl unit vibrations in hydrohematite. Some of these bands, e.g. 1687-1674, 1643-1640, 888-884 and 880-798 cm⁻¹, completely disappeared at a heating temperature of > 230°C, while others alter the corresponding hematite bands.

IR absorption spectrum of French ochre, depicted in Fig. 2a, shows well-defined bands at above 3600 cm⁻¹ and 112, 1031, and 1008 cm⁻¹, attributable to kaolinite and hematite peaks at 537 and 469 cm⁻¹ and to goethite ones at 913 and 798 cm⁻¹. The peak at 694 cm⁻¹ may be due to maghemite. After thermal treatment (600°C for 24 h), the spectrum shows a significant peak broadening for kaolin and hematite bands. Again, goethite peaks disappear, and only the doublet at 778 and 798 cm⁻¹ remains, which is characteristic of quartz.

Voltammetry of the pigments

Figure 3 shows the SQWVs of: a) Spanish hematite, b) Orange French ochre, c) Italian umber, immersed into 0.10 M HCl. The SQWV of

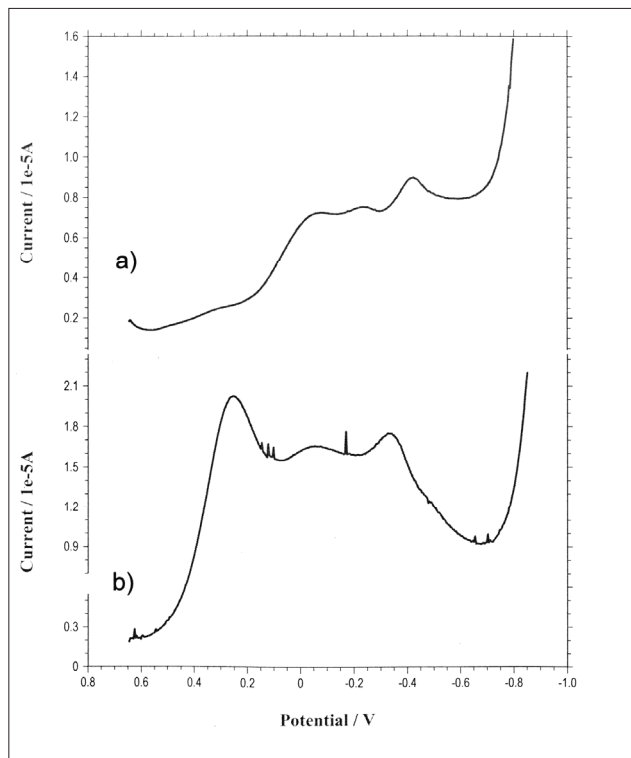


Figure 5. SQWVs of PIGEs modified with: a) Orange French ochre, b) Italian umber, both heated at 600 °C during 24 h, immersed into 0.10 M HCl. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

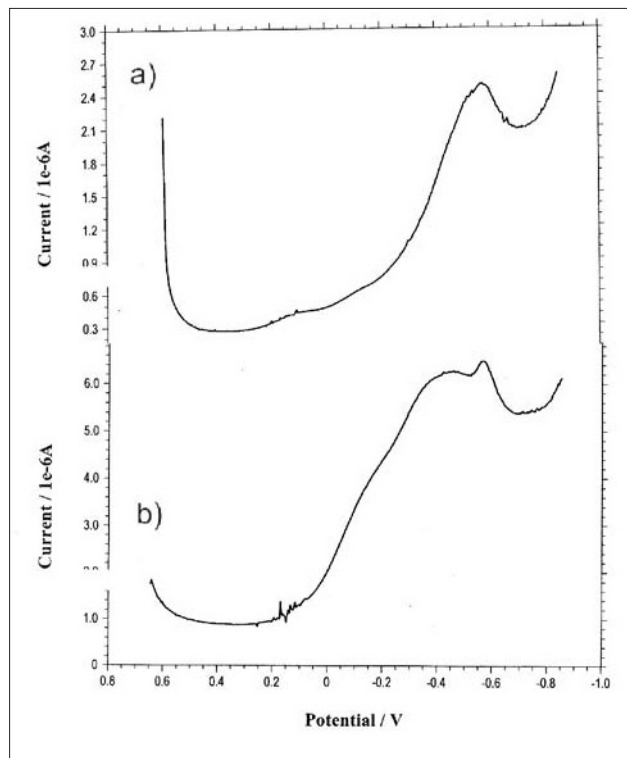
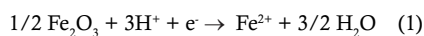


Figure 6. SQWVs of samples: a) TR4b, b) TR5b, immersed into 0.10 M HCl. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

Spanish hematite is representative of hematite-based pigments, consisting of a main reduction peak at -475 mV. The SQWV of French ochre shows overlapping peaks at -150, -250 and -425 mV, and is representative of ochres, siennas and clays. Finally, the voltammetric response of umbers is typically represented by Natural umber, for which peaks at +350, -100 and -250 appear.

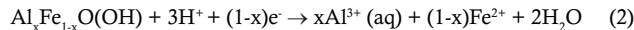
This voltammetry is consistent with that reported for iron(III) oxides and hydroxy-oxides and related materials (Mouhandess et al., 1982, 1984; Mancey et al., 1993; Encinas et al., 1994; Grygar et al., 1996, 1997). The overall electrochemical reaction can be described in terms of reductive dissolution processes which can be represented as:



for hematite.

The electrochemical reactions are phase-selective and their progress is affected by the pH and the presence of other chemisorbing ions and/or complexant species. The kinetics of the electrochemical process can be described on the basis of the model developed by Grygar (1996, 1997). Accordingly, the rate of reductive dissolution is driven by the detachment either via ion diffusion or a complexation reaction of metal centres from the reduced metal sites on the surface of solid particles.

In the case of earths, the position and shape of the voltammetric peaks depend on the average particle size and the homogeneity of the particle size distribution (Mouhandess et al., 1982, 1984; Mancey et al., 1993; Encinas et al., 1994; Grygar et al., 1996, 1997), so that the wider peaks correspond to less consolidated and probably more heterogeneous iron oxide materials (Grygar et al., 2002). For Al-substituted goethite materials, the reductive dissolution process can be described as:



As already reported (Grygar et al., 2002), the voltammetric peaks of the reductive dissolution are shifted cathodically on growing Al-for-Fe substitution, increasing particle size, and anodically with increasing departures of stoichiometry.

A comparison of SQWVs with the ATR/FTIR spectra revealed a strong correlation between voltammetric peaks and spectral features. The correlation of such spectral data with voltammetry suggests that the voltammetric peak at ca. +300 mV (I) can be attributed to a highly hydrated, amorphous portion of Fe oxides. Overlapping peaks between +50 (II) and -250 mV (III) can be attributed to goethite with a variable crystallinity and hydration degree, and hydrated hematite, whereas the peak ca. -450 mV (IV) can be attributed to crystalline hematite.

Pigment characterisation can be obtained by using two-dimensional diagrams from peak current data. These can be taken as shape-dependent parameters, as seen in Fig. 4, where the normalised peak current (relative to the higher peak in the voltammogram) of peak III, I(III), is plotted against the normalised peak current of IV, I(IV). Pertinent data are summarised in Table 1.

In this diagram, hematite-based, and Sienna and Spanish ochre pigments are concentrated in two regions of the diagram centred at the (1,0.35) and (0.50,1) points. Interestingly, French ochres occupy an intermediate position close to the (1,1) point, whereas umbers are localized further in the surroundings of the (0.3,0.5) position.

In all cases, SQWVs of pigments submitted to thermal treatments showed an enhancement of peak IV at the expense of all other peaks on increasing temperature. This can be seen in Fig. 5, where the SQWVs of: a) Orange French ochre, and b) Italian umber, after hea-

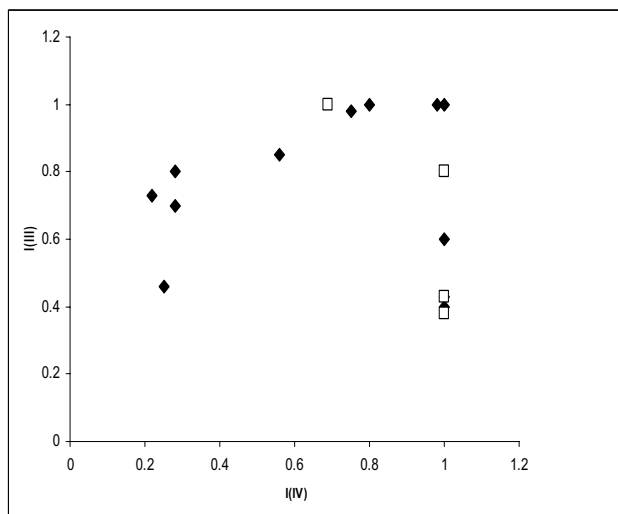


Figure 7. Two-dimensional diagram for earths and samples. Plots of I(III) vs. I(IV) for hematite-based pigments (solid squares), ochres (solid triangles) and umbers (solid rhombs). Squares correspond to samples from Sant Joan del Mercat church.

ting at 600°C for 24 h, are both shown. The above-mentioned feature is consistent with prior ATR/FTIR data, thus denoting that the crystalline hematite is formed from goethite and hydrated hematite forms.

Interestingly, the SQWVs of heated ochres and umbers are intermediate between those corresponding to the pristine pigments and those of the hematite-based ones. Thus, an insertion of shape-dependent parameters into diagrams enables heated pigments to be characterised. This is depicted in Fig. 4 where data of French ochre heated at 400, 600 and 800°C are shown. As expected, the diagram point for these pigments migrates along the $x = 1$ axis from its original position to those corresponding to typical hematite-based pigments.

Analysis of real samples

The IR absorption spectra of samples TR3a, TR4b, TR5b and TR6a is dominated by characteristic bands of calcite at 1387, 688 and 713 cm^{-1} . In samples TR4 and TR5, additional bands appearing at 797, 779, 670 cm^{-1} are found, which are ascribed to quartz. Bands at 3541, 3413, 1114, 670 and 605 cm^{-1} are associated with gypsum, and formed on the surface of the paintings as a consequence of the high level of SO_2 pollutant in the indoor church environment. Evidence of iron(III) oxide pigment is obtained from the weak band at 540 cm^{-1} appearing in the IR spectrum of sample TR5b and from the weak bands at 880 and 795 cm^{-1} occurring in the IR spectrum of sample TR4b.

Figure 6 shows the SQWV for samples a) TR4b, and b) TR5b in contact with 0.10 M HCl. In the first case, a hematite-type profile was obtained, where peak I at -0.45 V prevailed largely over the other voltammetric signals. A similar voltammogram was recorded for sample TR3a. In contrast, the SQWVs of samples TR5b and TR6a present a well-defined signal at -0.20 V, which is characteristic of ochre-type pigments. It should be noted that all voltammograms are distorted by the presence of a sharp peak at -0.55 V, corresponding to the reduction of lead white, an ubiquitous component of these samples.

An insertion of peak current data into a two-dimensional peak current diagram is shown in Fig. 7.

The positions occupied by sample data points in this diagram indicate that samples TR3a and TR4b consist of hematite pigments, while sample TR5b is a non-thermally damaged ochre-type pigment. Remarkably, sample TR6a occupies an intermediate position in the diagram between those of typical hematite pigments and ochre-type ones. Elec-

trochemical data indicate that this sample was probably submitted to a significant thermal stress, resulting in a significant goethite with hematite transformation. Pertinent peak current data are summarised in Table 1.

FINAL CONSIDERATIONS

Earth pigments provide well-defined spectral and voltammetric responses that are representative of their mineralogical composition. Despite the weak features from earth pigments appearing in the IR absorption spectra of real samples, which are dominated by the calcite, FTIR spectroscopy and SQWV data for pigment-modified electrodes in contact with 0.10 M HCl can be correlated to assess the presence of goethite and hematite with different degrees of crystallinity and hydration. Two-dimensional diagrams using shape-dependent peak current data enables an unambiguous characterisation of hematite-based pigments, ochres and siennas, French ochres, and umbers.

Thermal treatment of pigments determines significant changes in their spectral and voltammetric responses. At temperatures above 600°C, hematite-based signals are considerably enhanced in relation to goethite and hydrated hematite forms. The use of voltammetric peak currents allows us to distinguish between pristine hematite-based pigments and heated ochres and umbers.

The application of this methodology to samples from the Santos Juanes church allows us to characterise the presence of hematite-based, ochre-based non-damaged pigments and thermally damaged earth pigments in several samples.

ACKNOWLEDGMENTS

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Versión española

TÍTULO: *Análisis de los pigmentos tierra en los frescos de Palomino de la iglesia de Los Santos Juanes en Valencia (España) por voltamperometría de estado sólido y espectroscopia FTIR*

RESUMEN: *Se ha utilizado una combinación de voltamperometría de estado sólido y espectroscopia FTIR en modo de reflectancia total atenuada para la identificación de pigmentos de tipo tierra en muestras de los frescos ejecutados por Antonio Palomino (1707) en la bóveda de la iglesia de Los Santos Juanes de Valencia (España). Tales frescos sufrieron considerables daños durante los incendios que tuvieron lugar durante la guerra civil española en 1936 dando lugar a graves alteraciones químicas y cromáticas.*

PALABRAS CLAVE: *voltamperometría de estado sólido, espectroscopia FTIR, pigmentos de óxido de hierro, pigmentos tierra, iglesia de Los Santos Juanes, Antonio Palomino, pintura mural*