

Identification of copper-based green pigments in Jaume Huguet's Gothic altarpieces by Fourier transform infrared microspectroscopy and synchrotron radiation X-ray diffraction

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The scientific investigation of ancient paintings gives a unique insight into ancient painting techniques and their evolution through time and geographic location. This study deals with the identification of the green pigments used by one of the most important Catalan masters in Gothic times, Jaume Huguet. Other pigments and materials have also been characterized by means of conventional techniques such as optical microscopy, scanning electron microscopy and Fourier transform infrared spectroscopy. Synchrotron radiation X-ray diffraction has been used to produce maps of phases at a spatial resolution of 100 µm across chromatic layers.

Keywords: X-ray diffraction; Fourier transform infrared spectroscopy; Gothic altarpieces; Jaume Huguet; green pigments; copper compounds.

1. Introduction

The scientific investigation of ancient paintings gives a unique insight into ancient painting techniques and their evolution through time and geographic location. The present study is part of a comprehensive study of the materials including preparation, pigments, bindings and alterations as well as the painting techniques used by one of the most important Catalan masters of the Gothic times, Jaume Huguet (born ca 1415, Valls; died 1492, Barcelona) (Salvadó, 2001; Salvadó *et al.*, 2001). This study deals with the identification of the green pigments used by Jaume Huguet. Other pigments and materials were characterized by means of conventional techniques such as optical microscopy (OM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) (Salvadó, 2001). Nevertheless, in the case of the green pigments, although all of them are identified by SEM to be copper compounds, the small quantity of material available, the use of mixtures of compounds and the presence of low-crystalline compounds had thus far frustrated their identification. Owing to the high complexity and difficulty of their identification with conventional techniques, synchrotron radiation XRD was used to take advantage of properties such as the high intensity and penetration of the beam, small beam footprint and fast data-collection time (Pantos *et al.*, 2002; Tang *et al.*, 2001). The high brilliance of the synchrotron radiation X-rays opens the possibility for scanning cross sections of the samples. This can supply important

and definitive information on the nature of the copper-based green pigments.

1.1. Historical background

During the 14th century AD, the crown of Catalunya and Aragón, and Barcelona in particular, had an important presence in Mediterranean commerce. The economic, social and cultural life of the city flourished throughout the 14th century and the local artists were influenced by foreign fashions and techniques through the Mediterranean commerce. Although some political and social crisis reduced the importance of Barcelona, during the 15th century the city attracted some of the most important Gothic Catalan painters. Among them, Jaume Huguet was one of the most important artists of the period. His works fall between tradition (international Gothic style) and innovation (Flemish Renaissance) characteristic of the second half of the 15th century. In his time, Huguet was well known and he obtained some of the most important contracts for painting many religious artworks, mainly in the form of altarpieces. The paintings are characterized by a fine brushwork and a high control of the materials (pigments and binders). The play of colours of Huguet's paintings reflects a high level of knowledge of the materials and painting technique. Previous studies (Salvadó, 2001; Salvadó *et al.*, 2001) have provided evidence for the use of several natural pigments, namely, azurite, cinnabar, clays, haematite, and also of synthetic pigments, either inorganic, like the yellow tin lead oxide, or organic, like the red lake. They were applied over the plastered wooden surface, mixed with white (lead carbonates) to control the saturation of the colour. The binding medium was identified to be a protein, and the finding of phosphorus in the media allows us to affirm that it has to be egg. Therefore, egg tempera was used to bind the pigments and paint, although in some particular cases, *i.e.* the blue azurite, the binding media used was different, *i.e.* animal glue.

The samples studied are from three altarpieces: *Retaule del Conestable* commissioned by Pere de Portugal when proclaimed Count of Barcelona and King of Aragón in 1464 (Capella de Santa Agata, Barcelona), *Retaule de Sant Abdó i Sant Senen*, dated in 1460 (Esglesia de Sant Pere, Terrassa) and *Retaule de Sant Bernadí i l'Angel Custodi*, initiated in 1462 (Museum of the Cathedral of Barcelona) (Generalitat de Catalunya, 1993; Sureda Pons, 1994). Fig. 1 shows one of the plafonds belonging to the *Retaule del Conestable* from which samples were taken.

1.2. The green copper pigments throughout the history

The synthetic copper-based green pigments are compounds obtained by the corrosion of copper or copper alloys exposed to vinegar vapours. The process used in antiquity is described by ancient authors even though there is not much conclusive evidence of their application in the painting at that time (Rinaldi *et al.*, 1986). Vetruvius (Alianza Forma, 2000) explains in his treatise that in Rhodes these copper-based green pigments (*aeruca* or *aerugo*) were prepared from a copper plate placed on a base of twigs kept in a receptacle made of terracotta where vinegar was added. This procedure produced basic copper acetates (copper acetate hydrate). The pigment is normally referred as *verdigris* and both Cennino Cennini in his *Libro dell'Arte* (Brunello, 1997) and Leonardo da Vinci in his *Treatise on Painting* (Garcia, 1980) remarked on its instability. To make it more stable, Cennini recommends grounding it down with vinegar (in another treatise he also recommends treading it with vinegar). This treatment transforms the basic copper acetates into copper acetates which are more stable. Other traditional procedures for obtaining *verdigris*

include some modifications of major or minor importance to this method (temperature, additives).

A different procedure for obtaining green pigment which could give different copper compounds is given in the treatise of Theophilus, *De Diversis Artibus* (Escalopier, 1996; Hawthorne & Smith, 1979). The process described consists of smearing copper plates with honey and salt (sodium chloride) and exposing them to vinegar vapours in a sealed receptacle. In this study we reproduce these procedures and we demonstrate that a mixture of different copper-based compounds, such as acetates, basic chlorides and carbonates, is obtained. We will see that different mixtures of compounds are obtained depending on the conditions of production.

It is worth noting that a great diversity of green copper compounds may be obtained by modifying the recipes. So far, no detailed study has been undertaken of the copper compounds used and the connection with different manufacturing techniques through history. Nevertheless, some studies have started to produce reference data of green copper compounds and to associate them to the chronology and geography (Scott, 2000; Naumova & Pisareva, 1994). However, the lack of historical information on the use of these compounds does not allow us to relate the green pigment used by Jaume Huguet to any specific technological tradition or innovation.

2. Experimental

2.1. Reference materials

In order to obtain original copper pigments to compare with the ancient paintings, a set of materials, either mineral or synthetic, were prepared and analysed. Table 1 shows the chemical formulae, origin and main characteristics of the materials prepared. The compounds studied are copper carbonates (mineral and synthetic), copper acetates [synthesized following the *Vetruvius Treatise* (Alianza Forma, 2000)] and a mixture of copper compounds obtained following the ancient recipes given in the *Theophilus treatise* (Escalopier, 1996; Hawthorne & Smith, 1979). It is worth mentioning that the ancient recipes quite often give a mixture of compounds including copper acetates, chlorides and carbonates showing low particle dimensions, sometimes of amorphous nature. This is important, as this low crystallinity appears as one of the main difficulties in identifying ancient pigments. The synthetic materials S1 and S3 are commercial reagents, S2 is a mineral, and S4, S5, S6 and S7 are obtained following ancient recipes. The materials are obtained in powder form in all cases.

2.2. Sampling of Huguet's green paintings

The sampling of green paintings includes some of the most important altarpieces of Jaume Huguet: eleven samples from the *Retaule del Conestable*, five from the *Retaule de Sant Abdó i Sant Senen* and one from the *Retaule de Sant Bernadí i l'Angel Custodi*.

Of necessity, the samples are of small size, less than 1 mm² and include some plaster

substratum, several chromatic layers (thickness between 10 and 100 µm each), alteration and contamination surface layers (thickness less than 2 µm). Normally, two preparations were made: fresh-fractured fragments and polished cross sections. To prepare the cross sections, the samples are embedded in polyester resin polymerized by a peroxy organic catalyzer under low humidity conditions, cut with a diamond saw of thickness 0.1 mm and polished with diamond paste. Cross sections and fragments were first observed by OM. Part of one polished cross section was carbon-coated and observed by SEM and analysed for elemental composition using an energy-dispersive X-ray detector (EDX) attached to the microscope. Fig. 2 shows typical OM and SEM images showing that the green pigment is heterogeneous and contains a wide variety of particles of different size (<1–10 µm), morphology and colour (dark green, light green, blue). The analysis has shown the presence of copper in association with chlorine in all the samples. Moreover, in some of the samples, particles containing just copper are also found, but we have to consider that the EDX detector cannot detect elements of lower atomic number than Na.

2.3. Analytical techniques

In this study we develop a methodology for the identification of the copper compounds by means of microscopic techniques able to deal with the extremely small samples available. Synchrotron radiation X-ray diffraction (SR-XRD) and FTIR able to work on microscopic samples were chosen as suitable techniques for the identification of the compounds.

FTIR was performed with a BOMEN MB-120 instrument coupled to a Spectra-Tech IR-Plan microscope. In all the cases small particles of the samples were placed in a diamond cell for the analysis. SR-XRD measurements were taken at station 9.6 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. SR-XRD enables us to work with a very intense beam (*ca* 30 s collecting time during single-bunch mode

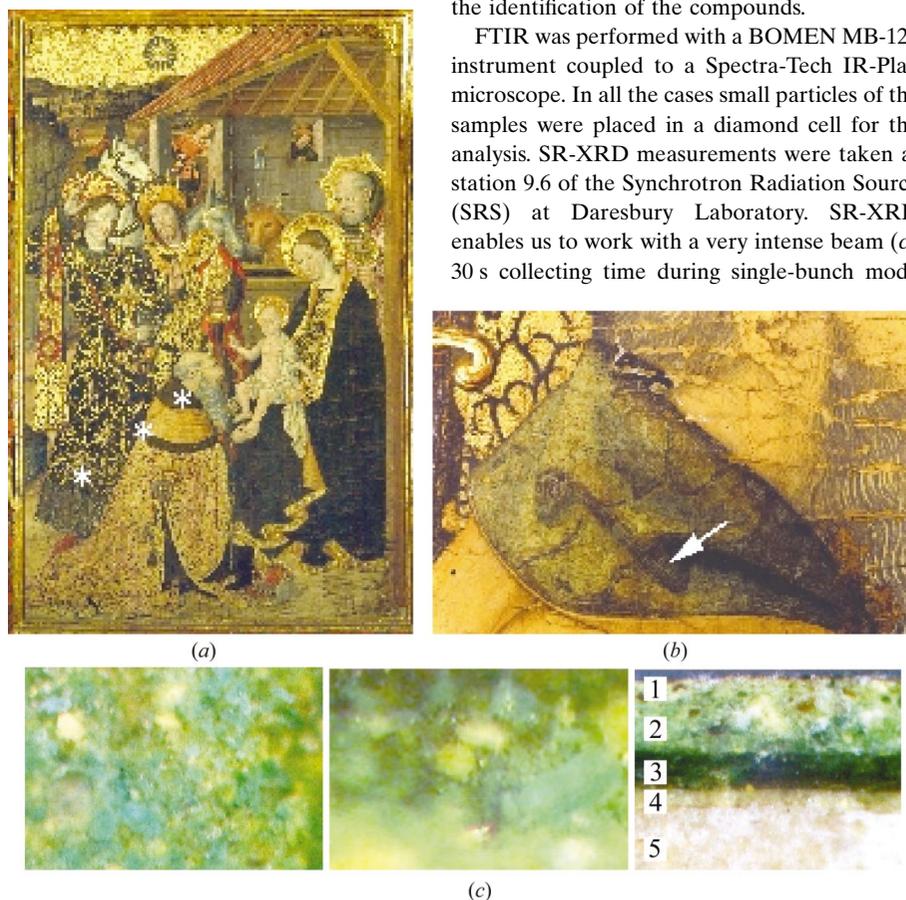


Figure 1 (a) Central plafond (Epiphany) from the altarpiece of the *Conestable*. Asterisks indicate some of the points from which samples were extracted (photography from 'Serveis de Restauració i Bens Mobles de la Generalitat de Catalunya'). (b) Detail of one of the points from which a sample was extracted. (c) Optical microscopy image of the sample, detail of fragment and section. (1: alteration layer; 2, 3 and 4: green chromatic layers; 5: preparation layer).

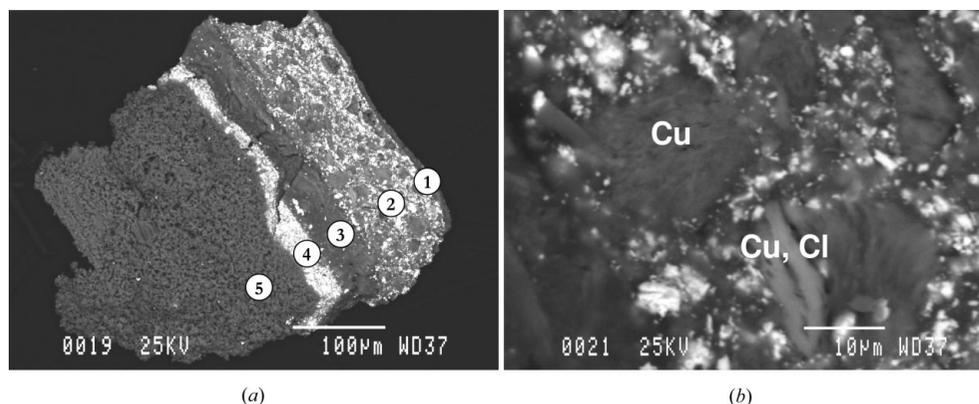


Figure 2 Backscattered electron images obtained at the SEM at 25 kV and 1 nA of the same sample as Fig. 1. (a) Fragment where the stratigraphy is shown. (1: alteration layer; 2, 3 and 4: green chromatic layers; 5: preparation layer). (b) The particles belonging to the green chromatic layer are shown. The lighter particles, $< 3 \mu\text{m}$, have Pb and Sn and the darker particles have Cu and some Cl.

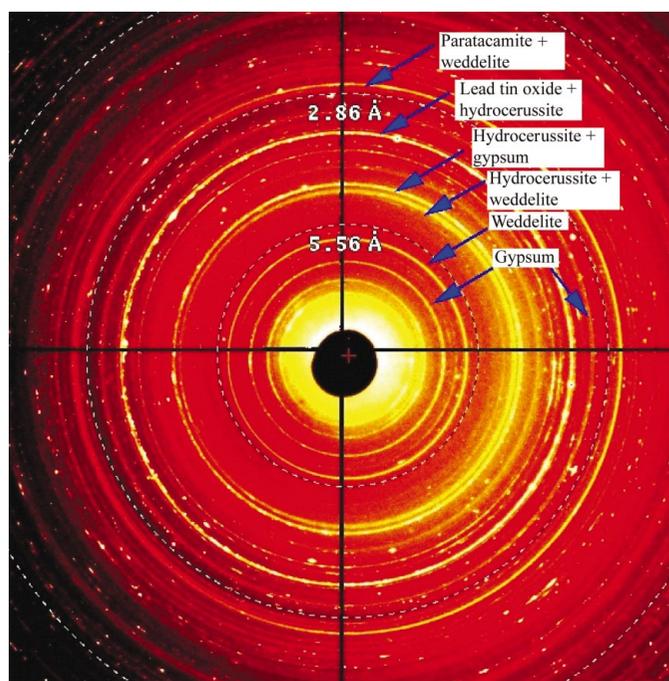


Figure 3 An example of a diffraction pattern as collected by the CCD detector. Image size 2300×2300 pixels. Two resolution rings at 5.56 and 2.86 Å are shown together with the identification of some of the phases. Data were collected, typically to 1.3 Å, by setting the CCD detector to the appropriate distance from the sample. All the reflections were used to identify the phases. Generally speaking, the spotty reflections are related mainly to gypsum while the rings corresponding to weddelite, white lead and yellow pigments are very homogeneous indicating fine particle size for these phases. The rings corresponding to some of the compounds forming the green pigment contain some spotty reflections indicating the presence of some large crystallites as well as fine-grain ones.

and beam current $< 20 \text{ mA}$ for these measurements, it can be as little as 2 s in multibunch mode), with high-energy (*i.e.* high-penetration) photons ($E = 14.25 \text{ keV}$, $\lambda = 0.87 \text{ \AA}$), and a very small ($100 \mu\text{m}$) beam footprint defined by the aperture of a cylindrical collimator. The XRD patterns are collected in transmission geometry by a QUANTUM-4 CCD area detector. A microscope alignment system

allowed the location of the beam on the desired part of the sample. A translation stage attached to the φ -axis of the goniometer permitted the collection of two-dimensional compound maps of the thin sections. The diffraction pattern of the resin was subtracted before data analysis. The fragments were held on an adhesive tape while powders were supported in a 0.5 mm quartz capillary which could be oscillated by a given angle about the φ -axis during exposure. In all cases the background scatter due to the support and air was subtracted before the data analysis using the ESRF package *FIT2D* (Hammersley *et al.*, 1996). Fig. 3

shows a typical diffraction pattern showing continuous (small particle size) and speckly (larger crystallites) diffraction rings superimposed on the resin + air diffuse background.

3. Results and discussion

3.1. Reference materials

An overview of the phases determined is given in Table 1. The reference JCPDS (Joint Committee for Powder Diffraction Standards; Raven, 1999) PDF cards used in the phase identification are given. The FTIR absorption bands are also given for the different compounds identified. It is important to note that the main differences observed by FTIR between a synthetic copper carbonate and the mineral malachite are not the position of the absorption bands but their shape.

The most important result from this work relates to the materials obtained by following the ancient recipes. The products appear normally as a complex mixture of copper compounds, including chlorides, acetates and carbonates. It is noteworthy that quite often these compounds are not very crystalline, either because of the small particle size or because of their intrinsic amorphous nature. The production of copper acetates and copper chlorides was expected to evolve from the original compounds used. We believe that the presence of different chemical structures for the copper chlorides such as paratacamite, atacamite and calumetite is an extremely interesting and important result. That the different fractions appear depending on the method of preparation is also an important result, which perhaps explains the wide variety and mixture of copper compounds found in the ancient paintings. Moreover, the production of copper carbonates was rather unexpected and it must result from the reaction of the mixtures with the atmosphere. This is also a very important result, because the presence of copper carbonates is normally attributed to the use of the mineral malachite. This demonstrates that copper carbonates with the structure of malachite may also be obtained by synthesis.

3.2. Ancient painting samples

A summary of the phases identified in the ancient paintings is given in Table 2. The information is obtained either by SR-XRD or micro-FTIR microspectroscopy. The information on the ancient samples obtained by FTIR is related to both the inorganic compounds present and to the nature of the organic binding medium. The binding

Table 1
Reference materials.

Sample	Compound	Comments†	Origin
S1	Cu ₂ CO ₃ (OH) ₂ Copper hydroxide carbonate	XRD (72-0075) FTIR (428, 501, 520, 570, 713, 755, 820, 876, 1048, 1099, 1393, 1510, 3407, 3322)	Synthetic (Probus)
S2	Cu ₂ CO ₃ (OH) ₂ Copper hydroxide carbonate	Malachite XRD (83-1298) FTIR (427, 500, 524, 571, 712, 748, 822, 872, 1046, 1096, 1388, 1500, 3312, 3403)	Mineral
S3	Cu(CH ₃ COO) ₂ ·H ₂ O Copper acetate monohydrate	XRD (27-0145) FTIR (628, 691, 1032, 1051, 1353, 1422, 1440, 1600, 2941, 2988, 3269, 3374, 3474)	Synthetic (Zechii 0997)
S4	Cu(CH ₃ COO) ₂ ·H ₂ O Copper acetate monohydrate	Vinegar vapours over copper plate XRD (27-0145) FTIR (628, 691, 1033, 1051, 1354, 1422, 1445, 1600, 2943, 2988, 3272, 3374, 3474)	Green pigment Vitruvius
S5	Cu(CH ₃ COO) ₂ ·H ₂ O Copper acetate monohydrate	XRD (27-0145) FTIR (629, 690, 1033, 1051, 1353, 1422, 1445, 1602, 2941, 2990, 3271, 3373, 3474)	Green pigment Theophilus Open flask
S6	Cu ₂ (OH)Cl ₃ Copper hydroxytrichloride	Like atacamite and paratacamite XRD (atacamite 25-0269, paratacamite 70-0821, 23-0947) FTIR (848, 896, 951, 987, 1053, 3344, 3362, 3442)	Green pigment Theophilus Closed flask
	Cu(CH ₃ COO) ₂ ·H ₂ O Copper acetate hydrate	XRD (27-0145) FTIR (1033, 1053, 1356, 1435, 1442, 1608, 1622, 2943, 2991, 3274)	
	Cu ₂ CO ₃ (OH) ₂ Copper hydroxide carbonate	Synthetic XRD (72-0075)	
	Cu ₂ CO ₃ (OH) ₂ Copper hydroxide carbonate	Structure like malachite XRD (83-1298)	
	Cu(OH,Cl) ₂ ·2H ₂ O (?) Copper hydroxychloride hydrate	Structure like calumetite XRD (15-0669)	
S7	Cu ₂ (OH)Cl ₃ Copper hydroxytrichloride	Structure like atacamite XRD (25-0269) FTIR (849, 897, 916, 953, 989, 3340, 3442)	Green pigment Theophilus Closed flask

† The numbers given correspond to the JCPDS PDF cards for XRD and to the position of the absorption bands (cm⁻¹) for the FTIR.

Table 2
The different compounds identified in the ancient green paintings.

Formula	Name	Comment	Origin
CaSO ₄ ·2H ₂ O	Gypsum XRD (72-0596)	Substrate Surface contamination	
CaC ₂ O ₄ ·(H ₂ O) _{x > 2}	Weddelite XRD (75-1314)	Weathering	
PbCO ₃	Cerussite XRD (70-2052)	White pigment	Synthetic
Pb ₃ CO ₃ (OH) ₂	Hydrocerussite XRD (13-0131)	White pigment	Synthetic
SnPb ₂ O ₄	Lead-tin oxide XRD (75-1846)	Yellow pigment	Synthetic
SiO ₂	Quartz XRD (5-0490)	Contamination	
Cu ₂ (OH)Cl ₃	Paratacamite XRD (25-0269) Atacamite XRD (70-0821)	Green pigment	Synthetic
Cu(CH ₃ COO) ₂ ·H ₂ O	Copper acetate hydrate XRD (27-0145)	Green pigment	Synthetic
Cu ₂ CO ₃ (OH) ₂	Copper hydroxide carbonate XRD (72-0075)	Green pigment	Synthetic
Cu ₂ CO ₃ (OH) ₂	Malachite XRD (83-1298)	Green pigment	Synthetic
Cu(OH,Cl) ₂ ·2H ₂ O	Calumetite XRD (15-0669)	Green pigment	Synthetic

medium was identified to be a mixture of a protein and drying oils, as can be seen in Fig. 4. In the layers, EDS analysis at the SEM showed the presence of phosphorous, indicating that the protein should be related to egg yolk or whole egg.

It is important to note that the spectrum related to the whole painting results from an overlap of the absorption bands contributed by each component in the mixture of green compounds, binding

medium and other pigments. However, the FTIR microscope allowed us to focus on single particles and to obtain spectra related to just the green pigment. From the study of different samples, copper basic carbonate (malachite), copper hydroxychlorides (atacamite, paratacamite) and monohydrated copper acetates have been determined. The absorption bands were related to those compounds in agreement with reference data in the literature (Goldsmith & Ross, 1968; Dei *et al.*, 1998; Gettens & Fitzhugh, 1974; Farmer, 1974; Baraldi & Fabbri, 1981; Giangrande, 1987; Fuchs & Oltrage, 1990; Jones & Jackson, 1993; Kühn, 1993). Further details on the FTIR procedures and results will be reported elsewhere. We highlight here only the essential aspects as they relate to the complementary information derived from the two analytical techniques, keeping the focus on the SR-XRD work.

The absorption bands between 1560 and 1610 cm⁻¹ are due to the presence of copper acetate and correspond to the asymmetric stretching vibration of the C—O bond in the acetate group. The monohydrated copper acetate shows absorption bands at 3482 cm⁻¹ and 3378 cm⁻¹ which relate to water incorporated in the structure. This concurs with the XRD identification of copper acetate hydrate. The bands that appear below 1000 cm⁻¹ are related to the basic chlorides. These bands (800–1000 cm⁻¹ are the planar deformation modes of the —OH group) are not very intense and quite often do not appear well resolved. Nevertheless, when a band is observed in this region, the 3345 cm⁻¹ band characteristic of the hydroxyl group (stretching vibration) of these compounds is also observed. Fig. 4 shows an example of a well resolved spectrum of Cu₂Cl(OH)₃ (structure of paratacamite).

For the copper carbonates, the band assignment is not as straightforward as most of the bands overlap with those due to other inorganic compounds, with the organic binding medium, or do not appear at all well resolved. The 820 cm⁻¹ band was obtained in some

of the samples and in this case it was related to the basic copper carbonates (malachite). The egg yolk also has a band in this position but it is not as intense and it is wider. The 1048 cm^{-1} (O—H) and 1096 cm^{-1} (CO_3^{2-}) bands, and the band appearing between 1494 cm^{-1} and 1510 cm^{-1} (CO_3^{2-}) overlap with the binding medium bands. The internal vibration bands of the ion carbonate at 1390 and 1420 cm^{-1} overlap with the 1440 cm^{-1} ($-\text{CH}_3$) and 1421 cm^{-1} bands of the copper acetates (symmetric stretching C—O) as well as with those of the carbonate group of the white pigment (cerussite/hydrocerussite). The 3313 cm^{-1} and 3405 cm^{-1} absorption bands (O—H) were not unambiguously identified in any of the spectra obtained. Finally, the lack of resolution of the 875 cm^{-1} (CO_3^{2-}) band impeded the discrimination between the synthetic or mineral origin of the phases.

The FTIR results seem to indicate that different compounds were used. The results are not very conclusive because not all of the compounds are identified in the samples studied. What is very important is the identification of a mixture of egg protein and drying oils in the binding medium; this is characteristic of the green painting. The use of drying oil is specific to the green paintings as it has never been found in any other of the colours of the altarpieces studied.

Fig. 5 shows the SR-XRD patterns corresponding to a thin cross section of a sample of the *Retaule del Conestable*. The measurements were taken at different points of the section as marked in the figure. The painting shows different layers, the outermost layer showing a mixture of green compounds (atacamite, paratacamite, calumetite and copper mono-hydrated acetates) mixed with a yellow pigment identified as a lead tin oxide (SnPb_2O_4) and, in very low quantities, the white lead pigment (hydrocerussite). While measuring the inner chromatic layer, the green compounds appear mixed with a higher quantity of the white lead but not of the green or yellow pigment. This suggests the application of a first white layer, followed by a second one containing white mixed with green, and a third one containing green mixed with yellow. The substrate is gypsum. In all the layers we detect the presence of calcium oxalate monohydrate (weddellite), although it is more abundant

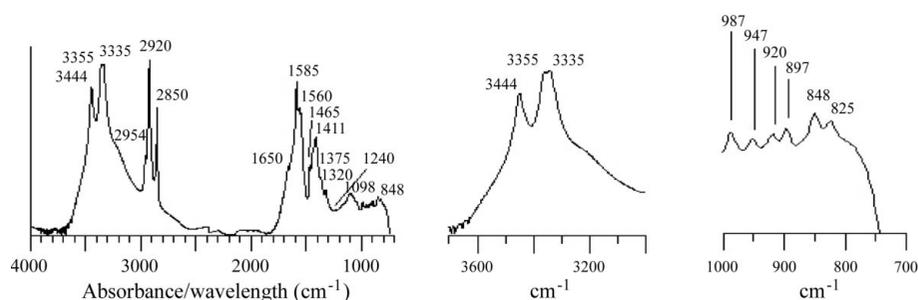


Figure 4 Microspectroscopy FTIR (125 scans, 4 cm^{-1} resolution) of the green chromatic layer, where $\text{Cu}_2\text{Cl}(\text{OH})_3$ (structure of paratacamite) bands at 3444 , 3355 , 3335 , 997 , 947 , 920 , 897 , 847 and 830 cm^{-1} are determined. The bands at 2954 , 2920 , 2850 , 1650 , 15409 , 1465 and 1240 cm^{-1} correspond exactly with bands found in the spectrum obtained after two years of ageing of egg yolk.

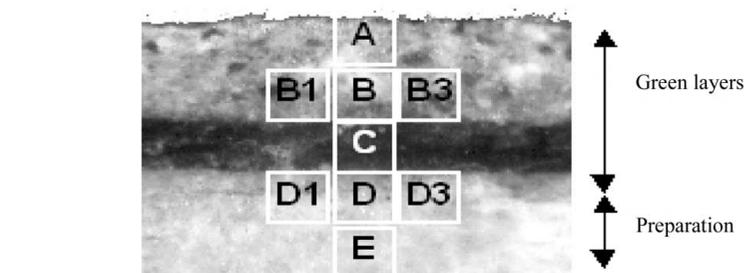
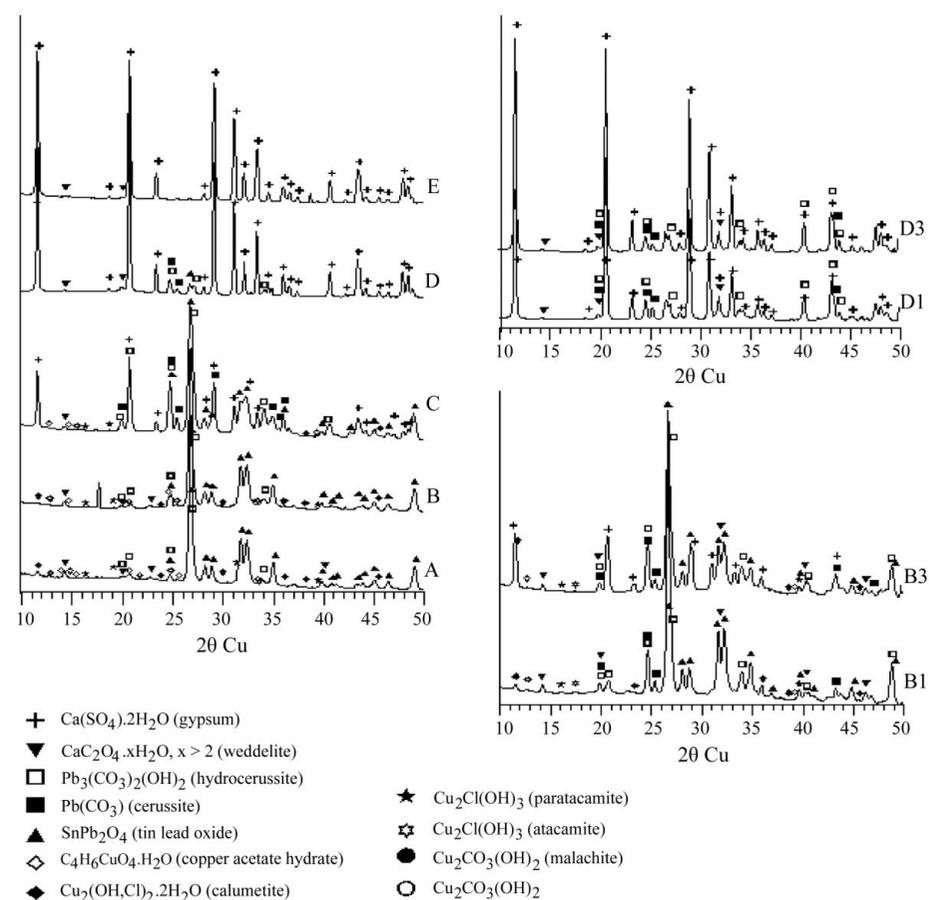


Figure 5 SR-XRD patterns corresponding to the cross section of a sample of the altarpiece of *Conestable* (beam footprint $100\text{ }\mu\text{m}$).

at the surface. We associate this compound with an alteration of the organic media, the egg protein and drying oil for the chromatic layers and the animal glue for the plaster support.

Fig. 6 shows a two-dimensional map of phases obtained from a cross section of a sample from *Retaule de Sant Abdó i Sant Senen*. The small footprint of the synchrotron beam made such mapping possible. As shown in the figure, one set of samples corresponds to the outer chromatic layers and a second set to a chromatic layer closer to the plaster substrate. The measurements on the top surface layer exhibit a strong amorphous background which may be related either to a thicker binding layer or to the presence of amorphous green phases. The outer chromatic layers contain basically green compounds (paratacamite?, malachite and synthetic copper basic carbonate) mixed with the yellow pigment and some small quantities of lead white pigment. The inner chromatic layers contain a higher level of lead white pigment (cerussite and hydrocerussite). There are no green compounds or yellow pigments. The results suggest that Huguet applied a first white layer with some yellow and a second layer of green mixed with yellow. The presence of weddelite is observed everywhere but predominantly at the surface of the painting layer.

Fig. 7 shows a series of measurement spots along a cross section of a sample from *Retaule de Sant Bernadí i l'Angel Custodi*. The chromatic layer closer to the outer surface shows a mixture of green copper compounds (malachite, copper acetate, paratacamite and calumetite) mixed with some yellow and white. One of the most

characteristic peaks which is related to calumetite (7.50 Å) overlaps with one due to gypsum. However, it is very clearly seen in the figure that the position of the peak is slightly displaced and both peaks are seen separately while approaching the plaster surface. This demonstrates the difficulty of resolving calumetite in the diffraction patterns, and the need for high angular resolution. As in the other samples studied, it is observed that the quantity of yellow colour mixed with the green pigment diminishes while approaching the gypsum support and that the white colour increases (especially the hydrocerussite). In this case, two chromatic sequence layers, a first layer of white mixed with some green and a second layer of green mixed with yellow, are found.

Fig. 8 shows two spectra of special interest, corresponding to a sample obtained from *Retaule del Conestable*. A relatively pure green mixture is obtained and all the diffraction peaks related to the different green compounds are shown: paratacamite, atacamite, calumetite, basic copper carbonate (synthetic) and copper acetate monohydrate.

In summary, Jaume Huguet used a green pigment which was synthesized following a procedure similar to that described by Theophilus. He mixed the green pigment with egg and drying oil and applied it by forming different layers over the plaster surface. Normally, the first layer contained white (a lead white pigment) mixed in some cases with some green; the second layer contained the green pigment mixed with yellow (a lead tin oxide). In all the paintings studied, weddelite is found especially on the outside surfaces of the painting but also in the plaster. This is a phase due to weathering related to the alteration of the organic binding media (egg and drying oils for the chromatic layers or animal glue for the plaster). Consequently, the painting technique, colours and their alterations are the same for all the altarpieces studied.

The green pigment itself shows a complicated mixture of compounds. The diffraction peaks corresponding to the different compounds are necessarily small and they always appear mixed with the diffraction peaks related to other colours. The relative intensities of the diffraction peaks do not always agree with the powder diffraction patterns, but this must be related to the fact that we did not rotate the sample and, consequently, some small crystals diffract with some of the crystallographic planes in 'preferred' orientation. In this respect, use of a 100 µm footprint, rather than much smaller footprint, can be considered as an advantage as more crystallites are contained within it. Some amorphous matter is found, especially on the outer chromatic layers. This may be due either to the presence of a thicker organic binding media or to the presence of green compounds of a small crystalline size or dissolved into the binding media.

Finally, it is important to note that the use of a drying oil has only been detected in the green paintings and, consequently, it seems that there have to be some technical reasons for its use in this case. This is important

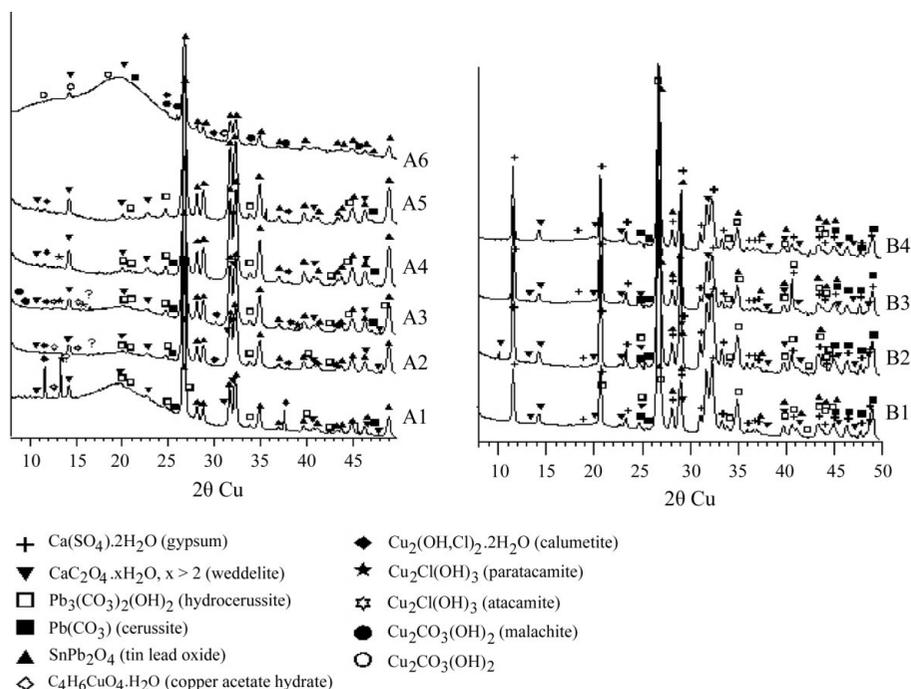


Figure 6
SR-XRD patterns corresponding to the cross section of a sample of the altarpiece of *Sant Abdó i sant Senén* (beam footprint 150 µm).

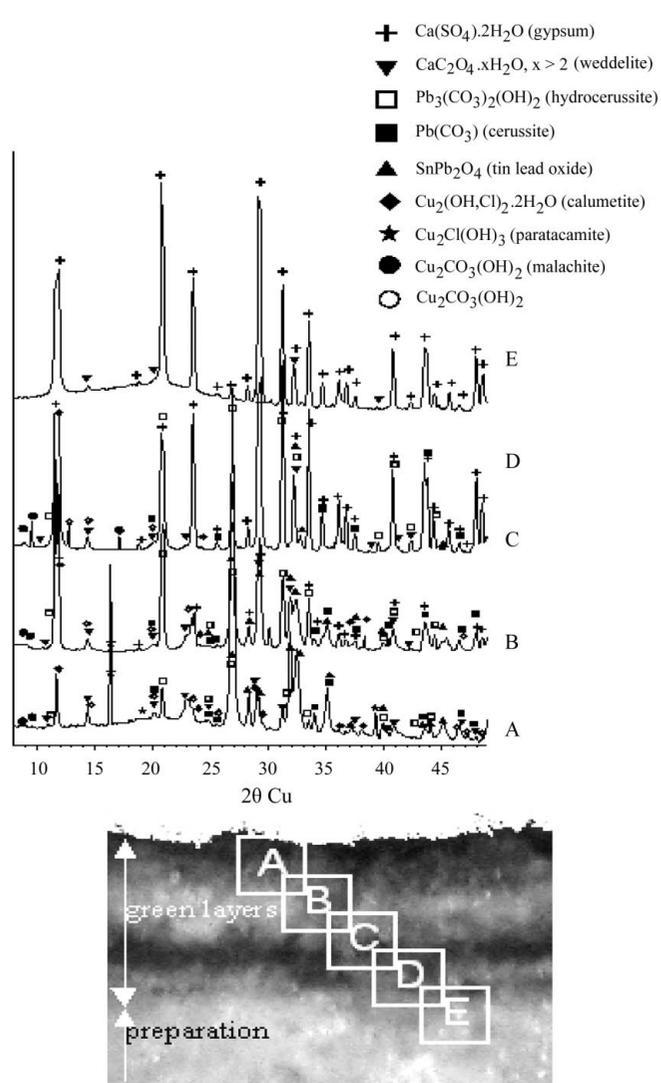


Figure 7
SR-XRD patterns corresponding to the cross section of a sample of the altarpiece of *Sant Bernadi i l'Àngel Custodi* (beam footprint 100 μm).

because it is the first documented example of the use of oil by contemporary Catalan Gothic painters.

4. Conclusions

The green pigments used by Jaume Huguet are found to be a mixture of green copper compounds synthesized following Theophilus' recipe. He mixed the green pigment with egg tempera and drying oils. Normally the paintings are applied in different layers containing lead white and also a yellow pigment identified to be a lead tin oxide.

Although SEM, FTIR and OM are complementary techniques which give an insight into the nature of the binding medium, the heterogeneity in colour or size distribution of the particles, SR-XRD has been of crucial importance in providing a secure identification of the green pigment and the painting technique. In this study, a beam footprint of 100 μm has been quite adequate in achieving the primary objectives. Even smaller footprint sizes can be obtained at third-generation synchrotron radiation sources on micro-imaging instruments (MacDowell *et al.*, 1998, 2001; Müller *et al.*, 2000; Somogyi *et al.*, 2001). Studies using such instrumentation on the submicrometre

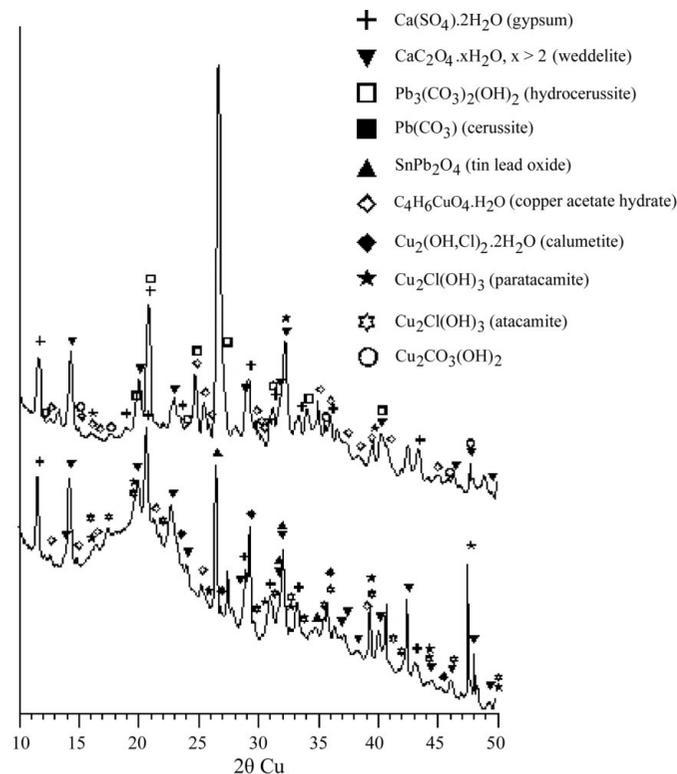


Figure 8
SR-XRD patterns corresponding to the cross section (green layer) of a sample of the altarpiece of *Conestable* (beam footprint 100 μm).

scale could be used to probe, for example, details of the interface between chromatic layers.

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