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Characterization of the binding medium used in Roman encaustic paintings on wall and wood†

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The characterization by means of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy and Gas Chromatography-Mass Spectrometry of the binding medium present in eight samples of Roman wall paintings coming from three archaeological sites in Spain and a sample of a Roman-Egyptian mummy portrait on wood showed strong evidence that the medium in all the studied samples was composed of beeswax and soap. These results suggest for the first time that Roman artists used in wall and easel paintings a water soluble encaustic paint of beeswax and soap. Experimental studies with a wax-and-soap technique showed that this painting technique allows reproduction of the physical characteristics of many Roman-Egyptian encaustic mummy portraits with greater accuracy than the hot wax encaustic paint and the alkali-treated encaustic paint often considered to be the painting techniques used in these portraits. Wax-and-soap encaustic also showed greater accuracy in reproducing the physical characteristics of Roman wall paintings than the fresco painting technique, generally thought to be the technique used to execute such paintings. This study suggests that wax-and-soap encaustic could be a common painting technique among Roman artists, and its composition could correspond to a lost ancient encaustic formulation searched for the last five centuries by many artists and researchers dissatisfied with the former reconstructions of the ancient encaustic painting technique.

Introduction

According to the ancient written sources, encaustic was the wax-based painting technique used by ancient Greek, Roman and Byzantine artists.[1–5] Encaustic was used in wall paintings[6–9] as well as in easel painting on wood and canvas,[10–14] on ceramic,[15] and in adding polychrome to sculptures and other objects of stone, metal and other materials.[16–19]

The ancient sources reflect the wide use of encaustic by painters in classical antiquity: it is practically the only technique mentioned in connection with the execution of works of art,[20–22] painters were called encausters or waxers, and the word ‘wax’ was synonymous not only with encaustic,[23–26] but also with painting.[27,28]

The use of encaustic paint was gradually abandoned during the Middle Ages, and this formulation was eventually lost. Encaustic was substituted by fresco in wall painting and by egg tempera, and eventually oil paint, in easel painting.

Uncertainty of the encaustic composition

The ancient sources do not make clear the exact composition of the wax paint. The most widespread theories suggest the existence of two types of encaustic: a hot encaustic made of beeswax – pure or mixed with resin – which was applied in the molten state, and a cold encaustic based on an emulsion of beeswax treated with an alkali, which could be used alone or mixed with other media.[29,30] However, these theories have not been fully confirmed, and the composition of the ancient encaustic remains subject to debate.[31–33] The next paragraphs summarize the main problems arising from both theories.

Hot wax encaustic

Molten wax colors are generally believed to have been used to paint the main group of ancient works considered to be encaustics: the Roman-Egyptian mummy portraits painted on wood and canvas known as Fayum portraits. However, many mummy portraits show brushstrokes that could hardly have been produced with the hot wax technique. This is true of the long, thin, and diluted brushstrokes, as well as some transparency effects observed in original paintings. Such brushstrokes suggest

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the use of a cold encaustic technique, as hot encaustic has an extremely fast drying time that requires thick brushstrokes, and lacks control over consistency and layer thickness. On the other hand, many portraits show strokes not painted with a brush but with a hard tool, often associated with the use of a molten wax technique, as this tool could be heated. However, these strokes could be also executed with a cold paint applied with a palette-knife.

Finally, it is important to bear in mind that the chemical analyses carried out on mummy portraits have not found evidence of the use of the hot wax encaustic painting technique. As an exception, one chemical study considered a mummy portrait to be painted with hot encaustic, based on the lack of alteration in the ester-to-alkane ratio, taken as an indicator for unsaponified wax in medium samples.[34] However, later studies indicated that wax saponification had little impact on the ester composition, being that the main factor was the degradation state of the medium.[35]

Cold wax encaustic

The composition of the ancient cold encaustic technique has been a constant source of controversy and disappointment.[36] Until now, researchers had proposed essentially two types of cold encaustic media: beeswax dissolved in organic solvents, and beeswax saponified with an alkali, which is often called Punic wax.

Encaustic with organic solvents seems to be currently ruled out as a Greco-Roman technique, since such solvents would not have been available in paint until the Middle Ages.[37]

The saponified wax technique finds its main support on the existence in Roman times of a type of wax called Punic wax, that could be, in the opinion of various authors, a saponified wax soluble in water.[38] This Punic wax would be prepared by boiling beeswax with an alkali (soda, potash, ammonium). In this process, the long-chain fatty acids in beeswax would form soaps by saponification with the alkali. The water-soluble soaps form an emulsion with the water-inmiscible components of beeswax – the wax esters and the *n*-alkanes (ref. 35) – that could be used as a water-soluble wax medium. The difficulty with this medium is that it shows the lack of cohesion and the resulting paint films crack and detach from the support when they dry, making this wax emulsion unfeasible as a paint medium.[39] Its use in paint formulation is reduced to an additive that could be incorporated in small amounts to a conventional medium – oil, casein, egg, gum, glue – and therefore the resulting technique cannot be strictly considered as encaustic, as its real binder is not beeswax.

An alternative theory to the nature of Punic wax suggests that it was not a water-soluble paint medium, but merely bleached beeswax,[40,41] insoluble in water, and whose interest for painters would lie in its property to produce brighter colors than untreated yellow beeswax. According to this theory, yellow beeswax would be repeatedly boiled in seawater or brine to which a little soda or niter is added. In this process, sodium chloride prevents the emulsion[42] and the beeswax rises to the surface to be skimmed while fatty acids in beeswax form water-soluble soaps that would be retained in solution.[43] The resulting clarified beeswax, composed mainly of wax esters and the *n*-alkanes,[44] is then exposed to the sun for complete bleaching.[45,46] Therefore, the presence of Punic wax or untreated beeswax in an ancient encaustic painting would not provide relevant data to determine whether the original paint formulation corresponded to a molten wax encaustic or to a cold encaustic.

Wax-and-soap encaustic

The regular detection of fatty acid salts in encaustic mummy paintings[47–49] together with the lack of cohesion of the alkali-treated beeswax might suggest that soap was a component added to beeswax instead of a by-product produced by saponification of the free fatty acids in beeswax. This theory was first postulated by the Spanish artist José Cuní, who developed in 1961 a cold encaustic technique based on beeswax and soap[50] while doing research on Roman painting techniques in Pompeii and at the Naples Archaeological Museum. The addition of a water-soluble soap to melted beeswax forms a stable wax-in-water emulsion that, unlike alkali-treated beeswax emulsions, does not crack while drying. Mixed with pigments, this binding medium provides a high quality water-based paint that can be applied at room temperature, very diluted or in thick brushstrokes, on wall, wood, canvas or paper.

Results of chemical studies of Roman wall paintings also suggest the use of this technique, as beeswax and soap were identified in Roman wall paintings from Pompeii and Herculaneum,[51–53] Marsala (Sicily), Mérida (Spain) and Complutum (Spain).[54] The presence of beeswax and fatty acids was also detected in paint on a Greek vase suggesting that wax-and-soap encaustic was also used in polychroming Greco-Roman pottery.[55] Despite these results, the theory of the existence in Greco-Roman times of a water-soluble encaustic of beeswax and soap, used both in wall paintings and in easel paintings on wood, had not been stated so far in the scientific literature.

Current theories on Roman wall painting techniques

During the last three centuries, determination of the painting technique used in Roman wall paintings has been subject to numerous controversies and conflicting results.[56] Recent literature usually has not considered encaustic as a possible binding medium for these paintings: alkali-treated encaustic, due to its lack of cohesion, cannot be used to reproduce a Roman wall painting, and hot encaustic is not a suitable technique for great size paintings and to produce the long, thin and transparent brushstrokes usual in Roman wall paintings.

Currently the most widespread theory considers Roman murals to be painted with fresco,[57,58] despite physical characteristics hardly compatible with those in fresco paintings. The next sections summarize the main discrepancies and inconsistencies.

Lack of *giornate* joints and presence of *pontate* joints

Unlike true frescoes from the Renaissance onwards, which are divided into *giornate* – relatively small areas of mortar painted in one day while mortar is still fresh (ref. 59 and 60) – which constitute the most recognizable feature common to fresco paintings, Roman paintings are executed on a lime mortar support divided into *pontate*.[61]

Pontate are great expanses of mortar that plasterers are able to apply in one go, and can be found under the paint layer in any modern wall plastered with gypsum, lime or cement. Joints between pontate are a characteristic of plastered walls painted a secco.[62]

In Roman wall paintings, *pontate* use to have a height of about 2 metres, corresponding to the levels of scaffolding, and their length extends from wall to wall and can reach up to 6 metres.[63] The fresco theory requires to explain how Roman artists could finish in eight hours – the time usually taken for the lime mortar to set – such extensive areas in complex and detailed wall paintings, whereas the great fresco masters from the Renaissance onwards, in spite of having trained teams of assistants, needed to divide the mortar surface into the smaller *giornate*.

Some studies have hypothesized that Roman artists could have used a set retarder that allowed to keep the mortar fresh for several days. However, the feasibility of painting with fresco on *pontate* using set retarders has not been able to be confirmed, and additives able to produce this effect have not been identified in analyses of mortars in Roman wall paintings.

Absence of tone variation around joints

Frescoes reveal a difference in tones across older and newer *giornate* section joints due to their characteristic decrease in color intensity during drying, which makes it very difficult to even the tone of an adjoining *giornata* already dried. The absence of tone variation around *pontate* joints in Roman wall paintings indicates that they were not painted with fresco.

High color intensity

The loss of color intensity produced during the set of fresco paintings[64] and the absence of an organic binder results in dull and matte colors. The high color intensity shown in many Roman wall paintings suggests that they could have been executed with paint containing some kind of organic medium.

Presence of pigments unsuitable for fresco painting

Roman wall paintings often show the presence of pigments such as white and red lead, malachite, azurite, cinnabar, orpiment and organic pigments,[65] which degrade in contact with lime and whose use technical literature on fresco advise against. The identification of such pigments in a wall painting is an indication that it would have not been executed on a fresh lime rendering.

Presence of white pigments made of calcium carbonate

The most common white pigments in Roman wall paintings are made of calcium carbonate. Traditional fresco paintings use lime instead of white calcium carbonate because lime brushstrokes keep the same degree of opacity and color in wet and dry conditions. Calcium carbonate pigments are transparent and hardly perceptible during application – mixed with water – and become opaque when dry, making impossible for the artist to anticipate how white the color will be once dry. Furthermore lead white pigment reacts with lime. Besides, Pliny[66] and Vitruvius[67] do not include lime among white pigments, which would suggest that fresco painting was not used.

Lack of color penetration in mortar

Unlike wall paintings executed on a dry lime rendering, fresco paintings show color penetration in the upper mortar layer. The absence of color penetration in the upper mortar layer is a common characteristic of Roman wall paintings[68] that suggests that paint was applied on a dry rendering.

Lack of rough impastos made with mortar

In fresco painting, paint is made with pigment and water. Due to this lack of an organic medium, impastos have to be done with mortar of lime and marble powder, which provides them with a rough surface absent in the impastos of Roman wall paintings.

Presence of beeswax

The fresco theory usually explains the regular presence of beeswax identified in chemical studies of Roman wall paintings as a result of a modern conservation treatment, but this explanation is unable to justify the beeswax and fatty acid soap in many samples taken from excavation and which have not undergone any conservation process.[52,69,70]

Motivation

The aim of this study is to carry out a chemical analysis of the binding medium in Roman wall painting samples and in Fayum portraits on wood that shed light in the on-going debate on whether the painting technique commonly used in the Roman wall paintings was fresco or encaustic, and which type of encaustic – molten wax, alkali-treated beeswax, emulsion of beeswax and fatty acid soap – could have been used by Roman artists in wall and easel paintings.

Materials and methods

In order to characterize the composition of the ancient encaustic medium and to determine its possible use in Roman wall painting, eight samples of three Hispano-Roman archaeological sites (Ampurias, Cartagena and Baelo Claudia), dating from the 1st century BC to the 2nd century AD, were studied.

The eight wall painting samples were retrieved directly from excavation, not having been subject to any conservation treatment in order to ensure the absence of modern materials in the samples. The binding medium of each sample was extracted using two different solvents, chloroform and water, with a Soxhlet extractor, and analyzed by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR) and Gas Chromatography-Mass Spectrometry (GC-MS).

In order to compare the composition of the binding medium used in wall paintings with the encaustic medium used in the Roman-Egyptian mummy portraits, a microsample of an encaustic mummy portrait on wood belonging to the Brooklyn Museum in New York dating from the 2nd century AD was analyzed by ATR FT-IR. Detailed information of the ancient painting samples analyzed is available in Table 1. Photographs of samples are available in the ESI†.

Reference samples of the possible encaustic paint media were prepared and analyzed by ATR FT-IR and GC-MS in order to compare their composition to that of the ancient paint samples. The reference samples were produced in the following way:

(1) Hot wax encaustic medium of pure beeswax: 20 g of white beeswax natural unbleached, manufactured by Gamblin, was melted at 85 °C and applied in the molten state on glass by means of a brush. After cooling at room temperature, the medium was transferred into a vial using a spatula.

(2) Hot wax encaustic made of white beeswax and resin: 20 g of white beeswax and 10 g of powdered mastic varnish crystals, supplied by New York Art Central Supply, were melted at 145 °C and applied in the molten state on glass by means of a brush. After cooling at room temperature, the medium was transferred into a vial using a spatula.

(3) Alkali-treated encaustic: 20 g of white beeswax, 1 g of sodium bicarbonate (Sigma-Aldrich, 99.5%) and 20 mL of distilled water were boiled and vigorously stirred. Once cooled down to room temperature, the resulting emulsion was applied on glass with a brush. The resulting film was left to evaporate overnight and then dried for 3 hours in the oven at 50 °C. After drying was complete, the medium – which was completely cracked – was transferred into a vial using a spatula.

(4) Encaustic medium of beeswax and linseed oil soap: 20 g of white beeswax, 20 mL of distilled water and 5 g of linseed oil potassium soap – handmade in the 1980s by José Cuní with cold pressed linseed oil and potassium hydroxide – boiled and vigorously stirred. Once cooled down to room temperature, the resulting emulsion was applied on glass with a brush. The resulting film was left to naturally dry overnight and then dried for 3 hours in the oven at 50 °C. After drying was complete, the paint film – which did not show any cracking – was transferred onto a vial using a spatula.

(5) Encaustic medium of beeswax and olive oil soap: 20 g of white beeswax, 20 mL of distilled water and 20 g of black olive oil potassium soap manufactured by Marius Fabre. The sample was then prepared as the previous ones.

It was planned to carbon date the samples using Accelerator Mass Spectrometry (AMS) in order to determine the approximate age of the binding medium in ancient samples. Two Roman wall painting samples were chosen for this analysis.

Finally, in order to verify the reliability of the chemical results, an experimental study of the original binding media was carried out which would allow the performance of the reconstructed painting techniques as artists' materials and their capability to reproduce the physical characteristics of the original paintings to be known.

Binding media extraction

A spatula was used to scrape, from the lime mortar support of the Roman wall painting samples, part of the paint layer, which was then ground into a fine powder by means of a mortar and pestle. Only a small portion (less than 25%) of the painting sample surface area was removed during this process. This measure was taken to ensure that future tests could be performed on the samples.

In order to prevent any further carbon contamination in the AMS analysis than that which may have occurred prior to the sample acquisition, water was used as the solvent in the Soxhlet extractions instead of an organic solvent. Chloroform, a relatively unreactive solvent which shows good solubility for beeswax and is commonly used in extractions of encaustic paint media,[71,72] was also used to extract samples 3 and 8 since they achieved a small yield and chloroform proved to produce a larger yield, as discussed later in the Results and discussion section.

A Sigma-Aldrich 100 mL Soxhlet extractor apparatus was used to extract the organic binding medium from the inorganic

Table 1 Details of the ancient painting samples analyzed

Sample number	Origin	Date	Details
Roman wall painting samples			
1	Ampurias (Gerona, Spain)	1st century BC	Fragment from a stratum under a *tabernae* in area 04-CRI30-2208, *Insula* 30, excavated in 2004.
2	Ampurias (Gerona, Spain)	1st century AD	Fragment from *tabernae* in area 05-CRI30-31008 of *Insula* 30, excavated in 2005.
3	Ampurias (Gerona, Spain)	1st century AD	Fragment from *tabernae* in area 05-CRI30-31008 of *Insula* 30, excavated in 2005.
4	Ampurias (Gerona, Spain)	End of 1st century to first half of 2nd century AD	Fragment from tabernae in area 92-F-2209 located west of the city's forum, excavated in 1992.
5	Ampurias (Gerona, Spain)	End of 1st century to first half of 2nd century AD	Fragment from tabernae in area 92-F-2309 located west of the city's forum, excavated in 1992.
6	Cartagena (Murcia, Spain)	1st century AD	Fragment of the excavation unit 34.482 belonging to the abandonment level of the Roman house with sectile, west side of the perystile.
7	Cartagena (Murcia, Spain)	1st century AD	Fragment of excavation unit 34.399 belonging to a collapse level in the south wing of the perystile of the Roman house with sectile.
8	Baelo Claudia (Cádiz, Spain)	Early 2nd century AD	Fragment of stucco in interior belonging to area of private house (Casa del Reloj) located by the factory. Reg. no. CABC/CR/03/06.
Roman-Egyptian mummy portrait on wood			
	Fayum, Egypt	Second half of 2nd century AD	Portrait of a man. Encaustic and gilding on wood. Reg. no. 40.386. 43,8 × 19,7 cm. Brooklyn Museum, New York.

pigments and fillers. 125 mL of solvent was added to a round bottom flask along with some glass beads to promote even boiling. Two solvents were used throughout the experimentation, chloroform and HPLC reagent grade water.

The paint scraped from the sample was placed into a fiberglass extraction thimble. Approximately 150 mg of scraped paint was used in most cases, except for the two smaller painting samples (3 and 8) where approximately 100 mg were used.

The extractor was operated for 40 hours total, at five to seven hour intervals. After extraction was complete, rotary evaporation was used to remove approximately half of the solvent, so that 60 mL remained. A heated sonic bath for five minutes was used to dissolve extract on the flask walls. The bath was heated to 60 °C to treat the aqueous extracts and 40 °C for chloroform extracts. Then 10 mL of the unprocessed liquid extract were transferred to a vial for storage. The remaining liquid, approximately 50 mL, was poured onto two large watchglasses to allow the remaining solvent to evaporate. The water extracts were placed in an oven at 140 °C and allowed to dry overnight. The chloroform extracts were left in the fume hood to evaporate naturally over this time and then dried for fifteen minutes in the oven.

After drying was complete, the paint extract was transferred into a vial using a spatula and its mass was determined by subtraction; weight measurements of the vial were taken before and after its addition. This also allowed calculation of the extractor yield by dividing the dried extract mass by the mass of the scraped paint sample added to the extraction thimble.

Analysis by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR)

IR is an established technique for the analysis of beeswax, so this method was chosen to characterize the artwork which is believed to contain it.[73] A Smiths Detection Identify ATR FT-IR was used to analyze the samples. The eight dried extracts of ancient wall painting binding media and the reference compounds were directly analyzed as solids using the same method. Unlike Roman wall painting samples, which are of a relatively large size (between approx. 12 × 10 to 5 × 6 cm), the small size of the paint microsample of the Fayum portrait did not allow for extraction of the binding medium. Therefore, it was placed on a clean glass slide and analyzed with no further preparation. Thus, ATR FT-IR analysis of the medium may give results that are obscured by bands corresponding to inorganic compounds in the paint.

The method used for analysis took sixteen scans of each the background and the sample and scanned the full spectral range (650–4000 cm^{-1}). A camera embedded in the instrument was employed to make sure the dispersion of the solid was even upon lowering the probe.

Analysis by Gas Chromatography-Mass Spectrometry (GC-MS)

A Varian Saturn 2000 Chrompack GC/MS/MS with a CP-3800 Gas Chromatograph and a Varian CP7846 fused silica capillary column (25 m length, 0.32 mm I.D.) were used with ultra-high purity He gas (flow rate of 1.2 mL min^{-1}). The injection temperature was set at 250 °C, and the oven was programmed with a temperature gradient (see below) to range between 120 °C and 300 °C. The MS was set to have a solvent cut of 2 minutes and was set to EI ionization mode with a *m*/*z* range of 10–650.

Beeswax consists primarily of odd-numbered, straight chain hydrocarbons with a predominant chain length of C27–C33; linear wax monoesters and hydroxymonoesters with chain lengths generally of C40–C48; complex wax esters; and free fatty acids, most of which are saturated and have a chain length of C24–C32[74–77]. Fig. 1 shows the main chemical components of beeswax that were presently studied.

In order to identify the carboxylic acids present in the beeswax, the samples were treated with a derivatizing agent which caused esterification of these compounds and facilitated their detection. Boron trifluoride and methanol were used to esterify the samples. 10 mg of sample extract was weighed into separate 12 mL vials and 1 mL of hexane was added. The vial was then sonicated for ten minutes in a bath at 60 °C, opened and placed inside the fume hood to cool for five minutes. The content of one ampule containing 2 mL of the derivatization mixture, composed of 10% BF_3 by weight, was transferred to the vial containing the sample. At this point, 0.5 mL of 2,2-diethoxypropane was added as a water scavenger to react with water to form methanol and acetone. The vial was shaken for one minute and then sonicated and heated at 60 °C for fifteen minutes. When the vial was placed in the bath, two clear, immiscible liquid layers were present, and after a reaction had taken place the colors changed due to the creation of polymeric byproducts; the organic layer became a faint yellow color and the aqueous layer turned a brownish color. After this phenomenon had occurred, the vial was removed from the sonic bath and placed in the fume hood to cool for fifteen minutes. At this time, the vial was opened and 1 mL of hexane and 1 mL of HPLC grade water were added. The vial was resealed and shaken for five minutes. Aliquots of the organic layer were analyzed during experimentation with the analytical standards to determine the amount of time required for the reaction to reach completion.

1 mL of the organic layer was transferred to a 2 mL vial using a micropipette. Molecular sieve 3A pellets were added to the vial to absorb any water that may have been remaining.

In order to increase the relative size of the peaks of the desired compounds, the concentration of the esters in the solvent was increased by allowing the solvent to evaporate and reconstituting the remaining solid with 50 μL of chloroform.

The GC-MS method was developed using three analytical standards for beeswax (hexacosanoic acid, triacontanoic acid, hentriacontane) and then optimized for detection of the key components of beeswax using derivatized white beeswax. The

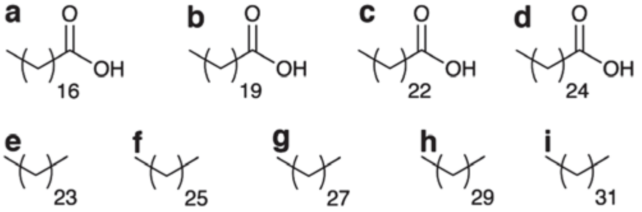

Fig. 1 Main chemical components of beeswax presently studied: octacosanoic acid (a), triacontanoic acid (b), tetracosanoic acid (c), hexacosanoic acid (d), pentacosane (e), heptacosane (f), nonacosane (g), hentriacontane (h) and tritriacontane (i).

final method that was determined to be optimal for testing the samples for beeswax had an initial oven temperature of 120 °C and a final oven temperature of 300 °C. The temperature ramp used for the first twenty minutes of the analysis was 7.5 °C per minute at which point the temperature ramp was reduced to 3 °C for ten minutes. When the oven reached 300 °C, it was held at this temperature for eight minutes to flush any remaining compounds from the column. This method took 38 minutes to complete. The analytical standards and the eight derivatized paint extract samples were tested using this method.

The gas chromatograms and mass spectra produced were analyzed in two ways to see if the key components of beeswax were present in the paint extracts. First, the peaks in the chromatogram were examined to see if components in the extract had the same retention times as those which had been determined of the beeswax components. Next, the mass spectra detected at each of the chromatogram peaks were examined to see if they matched those generated when testing the analytical standards and beeswax.

Analysis by Accelerator Mass Spectrometry (AMS)

Two samples were submitted to Beta Analytic, a laboratory in Miami, Florida, who offered an AMS service that could detect as little as 100 μg of final carbon in the sample. The first sample was a piece of painting sample number 4 in its original form, with paint on mortar. The painting surface was approximately 5 × 7.5 cm. The other sample submitted was 20 mg of the dried extract from the aqueous extraction of the same sample, number 4. This sample was used because it was the largest and had achieved a high extractor yield.

Results and discussion

Binding media extraction results

1. Aqueous extractions. Aqueous extractions were performed on the scraped paint from the eight wall painting samples. After determining the yields of the aqueous sample extractions and saving 10 mL of the 60 mL in the extractor for future analysis, the remaining liquid extract was oven dried to remove the water.

The extractor yields ranged from below 15% for samples 3 and 8 to a maximum of 25.58% for sample 7. The data show a trend, with the exception of sample 6: the smaller the mass of the sample the lower yield it produced. One possible explanation for this observation is that some of the finely ground paint may have gotten trapped in the pores of the extraction thimble and only the additional paint above this critical mass was affected by the extraction. This would be a reasonable explanation due to the observation that a 50% increase in mass from approximately 100 grams of samples 3 and 8 to approximately 150 grams for the other six samples led to just less than a 50% increase in extractor yield.

The extract concentration in the water was determined to range from 0.28 mg mL^{-1} for sample 8 to 0.74 mg mL^{-1} for sample 7 due to the variation in yield using the same amount of solvent. It is possible that this variance could be due to different ratios of paint to mortar in the sample which was extracted, or different ratios of medium to pigment in the paint. Another possible reason for the vast difference in extraction performance is the amount of time that the samples were extracted; samples 2 and 7 were operated for 42 hours and for one to two more sessions than other samples. The increase in the number of operation sessions caused additional variance in the total heating time due to the extraction, which occurred after turning the power to the heating mantle off each time. The slightly increased extraction time for samples 2 and 7 could have helped contribute to the increased yield.

Table 2 Summary of aqueous extraction results

	Mass of scraped paint/mg	Mass of dried extract/mg	Extractor yield (%)	Extraction time/h
Sample 1	150.4	34.2	19.75	40, 6 sessions
Sample 2	152.6	38.9	22.15	42, 8 sessions
Sample 3	100.2	17.1	14.87	40, 7 sessions
Sample 4	152.5	37.0	21.12	40, 6 sessions
Sample 5	151.0	29.3	16.90	40, 6 sessions
Sample 6	161.3	35.0	18.87	40, over 6 sessions
Sample 7	150.2	44.2	25.58	42, 8 sessions
Sample 8	100.9	16.6	14.34	40, 7 sessions

2. Chloroform extractions. Two chloroform extractions were performed under the same conditions so that the yields could be compared. Theoretically, if the paint contained beeswax, the yield should increase from that of the aqueous extraction when using chloroform since the wax is more soluble in this solvent than in water. Since samples 3 and 8 did not achieve as large a yield as the other six, they were chosen to be used for the chloroform extractions so that more extract could be obtained for analysis.

The extractions performed using chloroform as the solvent produced a much larger yield than in those where water was used to extract a slightly larger mass of scraped paint under the same conditions. The chloroform extract of sample 8 showed an increase of 71.1% from the aqueous extraction yield, and similarly the extract of sample 3 showed a 59.5% increase. This is a very large increase, though it is somewhat expected since the components of beeswax are much more soluble in chloroform.

Sample 8 achieved a yield of 24.54%, which was approximately the same as the maximum yield achieved by aqueous extraction, 25.58% for sample 3. This shows that chloroform was a much more effective solvent since just over 70 mg were used for the chloroform extraction while more than double this mass was used in the aqueous extraction which achieved a very similar yield. Based on this observation, it can be speculated that if chloroform were used on the samples with larger starting masses of paint, such as sample 3, the yield would have increased significantly as well. Overall, chloroform increased the extractor

Table 3 Chloroform extraction yields and comparison with aqueous extraction yields

	Mass of scraped paint/mg	Mass of dried extract/mg	Chloroform yield (%)	Aqueous yield (%)
Sample 3	70.4	16.7	23.72	14.87
Sample 8	70.9	17.4	24.54	14.34

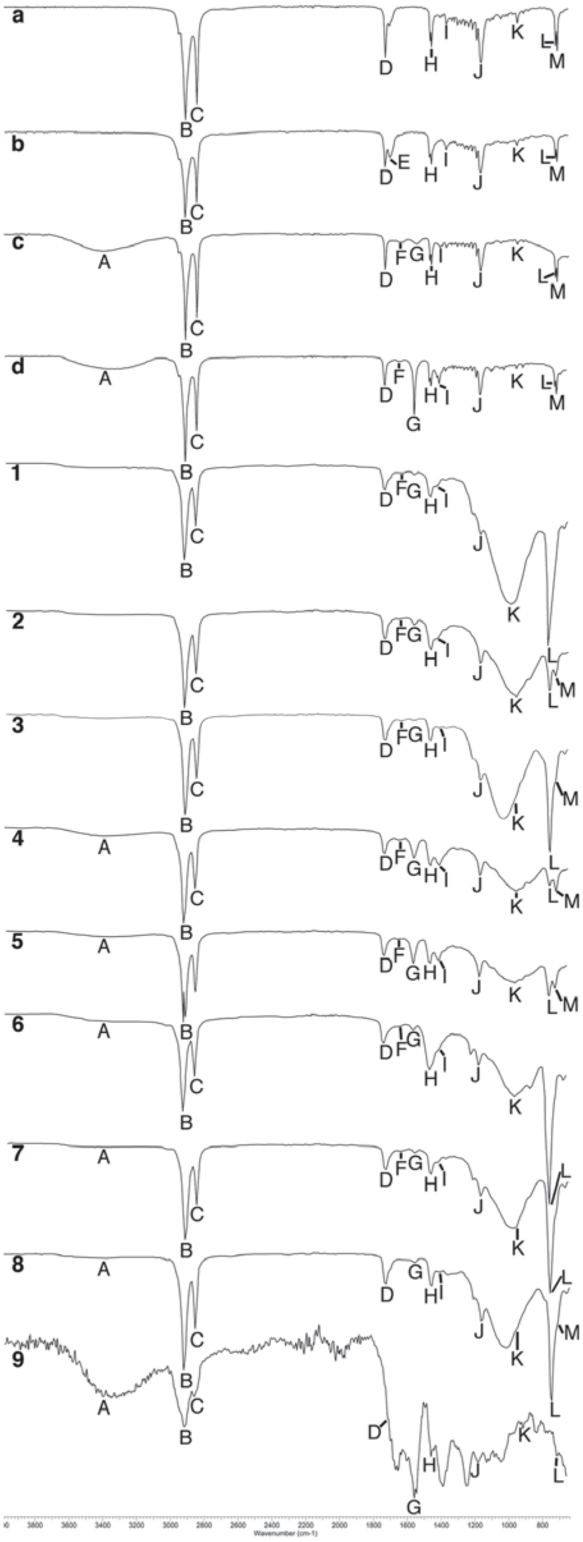

Fig. 2 Comparison between ATR FT-IR spectra of beeswax (a), beeswax with mastic resin (b), beeswax saponified with sodium bicarbonate (c), beeswax with black olive oil potassium soap (d), the binding medium in eight Roman wall paintings (samples 1–8), and the binding medium in an encaustic mummy portrait from Fayum (9). The binding medium extracts of the Roman wall painting samples and the Fayum portrait show alignment with bands characteristics of beeswax (B, C, D, H, I, J, K, L, M) and soap (A, B, C, F, G). Table 4 shows the compounds corresponding to the absorption bands identified.

yield and should be used as the preferred solvent if carbon contamination is not a consideration.

The results of the water and chloroform extractions are summarized in Tables 2 and 3.

ATR FT-IR results

The composition of the binding medium extracts of the Roman wall painting samples was analyzed using ATR FT-IR spectroscopy to determine the types of compounds present in conjunction with the results of GC-MS analysis. The resulting spectra were compared with those obtained with reference samples of beeswax paint media to determine the possibility of the presence of these media in the ancient samples.

Each of the eight dried extracts of the binding medium in the Roman wall painting samples was analyzed using ATR FT-IR spectroscopy. The spectra of the extracts were then compared with those of the reference products. The binding medium extracts showed similar absorbance bands to those of beeswax, along with the presence of other compounds as well.

The beeswax spectrum shows several characteristic peaks at the following wavenumbers: a doublet at 2914–2894 cm^{-1} (stretching vibrations of C–H groups), 1733 cm^{-1} (stretching vibrations of C–O–C groups), 1170 cm^{-1} (stretching vibrations of C–O–C groups), 956 cm^{-1} (bending of C–H groups), and a doublet at 780–719 cm^{-1} (nonplanar skeletal deformation vibrations of long-chain hydrocarbons).

The beeswax-and-mastic spectrum differs from pure beeswax mainly in the appearance of a carbonyl band at 1705 cm^{-1} due to resin esters.

Beeswax treated with sodium bicarbonate shows a decrease in the ester bands at 1733 and 1170 cm^{-1} and the appearance of two new bands produced by the saponified esters: a carboxyl band at 1548 cm^{-1} and an alcohol band at 1640 cm^{-1} that could be due to the formation of glycerol.

Soaps are characterized by ionized carboxyl groups whose absorption bands – depending on the type of soap analyzed – are in the regions between 1579–1540 cm^{-1} and 1430–1410 cm^{-1}. They also show a broad band between 3370 and 3232 cm^{-1} and a sharper band between 1630 and 1637 cm^{-1} due to glycerol produced by saponification of triglycerides. Compared to the spectrum of beeswax treated with sodium bicarbonate, the sample of beeswax and olive oil soap shows a sharper and stronger carboxyl band at 1561 cm^{-1}.

ATR FT-IR spectra of Roman samples (Fig. 2) show a doublet at 2914 and 2840 cm^{-1}, bands at 1733, 1109 and 956 cm^{-1} and a doublet at 780–719 cm^{-1} which are characteristics of beeswax; they also show a broad band at *ca.* 3320–3232 cm^{-1} and sharp bands at 1560, 1411 and 1109 cm^{-1}, consistent with the absorption bands of soap. The peaks in the single bond wavenumber range, below 1500 cm^{-1}, were present in the binding media, but were much broader indicating the presence of additional compounds with single C–C or C–O bonds. The origin of a large, broad peak at approximately 1000 cm^{-1} detected in the paint extracts was not identified and will be the subject of further studies.

The presence of resins, like mastic, pine balsam, dammar and sandarac, common resins in ancient Mediterranean cultures, was studied. The spectrum of these resins is characterized by a main

C═O stretching band in the region of 1678–1701 cm^{-1}. The absence of this band in the Roman wall painting samples was taken as an indication of the absence of resin.

The Fayum mummy portrait was then analyzed by ATR FT-IR spectroscopy. The portrait showed peaks aligned with absorption bands characteristic of beeswax (2914, 2849, 1733, 1560, 1170, 954, 915, 780 and 720 cm^{-1}) and soap (3345, 1560, 1462 and 1410 and 1109 cm^{-1}), together with some peaks not identified, which could be due to inorganic compounds, as pigments were not extracted. The peaks showing correspondence with beeswax and soap are consistent with those in the Roman wall painting samples (Fig. 2). Table 4 shows the compounds identified in the spectra.

GC-MS results

Analysis of the extracts using GC-MS was used to verify the presence of beeswax – pure, mixed with resin or treated with an alkali – and soaps in the Roman paint samples. Due to the nature of the carboxylic acids, derivatization was required to detect these compounds when using the GC-MS.

The chromatogram of beeswax is characterized by the presence of odd-numbered hydrocarbons with chain lengths of C_{21}–C_{33}, and saturated carboxylic acids with chain lengths of C_{24}–C_{30}. The admixture of mastic adds peaks of monoterpenes, sesquiterpenes and triterpenes at retention times of 19–23 min. Olive oil and linseed oil soaps are characterized by the presence of saturated and unsaturated fatty acids with chain lengths of C_{18}. Compared to the chromatogram of the beeswax saponified with sodium bicarbonate, the paint medium of beeswax mixed with linseed oil soap shows a significant increase in the amount of octadecenoic acid, providing a valuable indication to determine whether an ancient encaustic medium was composed of beeswax and fatty acid soap or of beeswax treated with an alkali.

Each of the eight dried binding medium extracts of Roman wall paintings was analyzed and the resulting spectra were then compared with that of the reference spectra of the possible encaustic paint media. All of the C_{21}–C_{33} hydrocarbons and C_{24}–C_{30} carboxylic acids characteristic of beeswax, as well as free fatty acids, were detected in five of the eight paint samples. These samples were the two samples extracted with chloroform (samples 3 and 8) and the samples extracted with water (samples 2, 4 and 5). Two of the remaining samples, 1 and 6, showed small chromatogram peaks at retention times corresponding to compounds determined in beeswax and fatty acid salts; however, the mass spectra were inconclusive about their identification.

Table 4 Compounds attributed to the absorption bands identified in the ATR FT-IR spectra

Band	Wavenumber/cm^{-1}	Functional group/ molecular motion	Chemical class
A	3390–3232	OH Stretching	Alcohols
B	2914	CH_2 Asymmetric stretching	Alkanes
C	2849	CH_2 Symmetric stretching	Alkanes
D	1733	C═O Stretching	Esters
E	1701	C═O Stretching	Esters
F	1542–1560	–COO$^-$ Asymmetric stretching	Carboxylates
G	1461	CH_2 Bending	Alkanes
H	1411	–COO$^-$ Symmetric stretching	Carboxylates
I	1170	C–O Stretching	Esters
J	956	C–H Bending	Alkanes
K	780	C–H Torsion band	Alkanes
L	719	CH_2 Rocking	Long chain alkanes

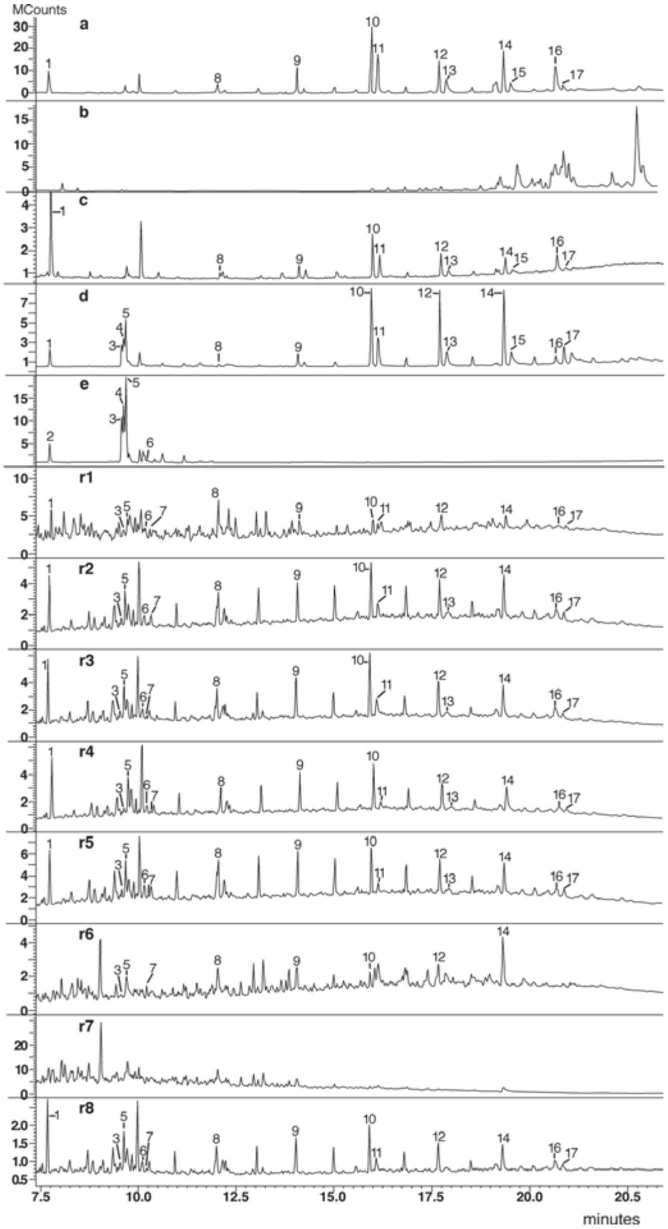

Fig. 3 Chromatograms of beeswax (a), mastic resin (b), beeswax saponified with sodium bicarbonate (c), beeswax with linseed oil potassium soap (d), linseed oil potassium soap (e) and the eight extracts of Roman wall painting samples (r1–r8) showing characteristic peaks of beeswax and soap. In all cases the *x*-axis shows retention times in minutes and the *y*-axis shows the total ion current (MCounts).

Sample 7 does not show any such evidence of these peaks. One possible reason for the inconclusive results of samples 1, 6 and 7, extracted with water, is that there was not a large enough quantity of binding medium in the extracts. The significant

Table 5 Identification of key components of beeswax and linseed oil potassium soap. Carboxylic acids were detected as methyl esters of the compounds listed

Peak label	Compound identification	Retention time/min	Mass detected (m/z)	Relative count[a]
1	Henicosane	7.750	269.6	0.19
2	Hexadecanoic acid	7.752	270.1	0.23
3	9,15-Octadecadienoic acid	9.612	294.0	0.53
4	9,12,15-Octadecatrienoic acid	9.654	292.2	0.67
5	6,11-Eicosadienoic acid	9.711	297.0	1
6	9,12-Octadecadienoic acid	10.247	294.0	0.03
7	9,15-Octadecadienoic acid	10.446	294.0	0.04
8	Tricosane	12.065	324.6	0.14
9	Pentacosane	14.690	352.6	0.47
10	Heptacosane	15.966	380.3	1
11	Tetracosanoic acid	16.152	382.1	0.72
12	Nonacosane	17.732	408.7	0.81
13	Hexacosanoic acid	17.901	410.2	0.40
14	Hentriacontane	19.367	436.8	0.80
15	Octacosanoic acid	19.549	438.2	0.37
16	Tritriacontane	20.705	464.9	0.72
17	Triacontanoic acid	20.901	466.3	0.22

[a] The relative counts were determined by dividing the ion current for a given peak by the ion current for the largest peak in that spectrum.

amount of fatty acids detected suggests that they were not produced through saponification of beeswax, but they were added to the beeswax medium in the form of soap. Roman samples do not show peaks that could be ascribed to terpenes, which seems to indicate that resin was not used in the ancient paint media analyzed. The significant amount of unsaturated fatty acids in Roman samples could suggest that the original soaps used in the paint media were produced with some kind of drying oil. However, further studies are necessary in order to accurately determine the types of oils or fats that could have been used in Roman wax paint formulations. Fig. 3 shows the chromatograms of beeswax, mastic resin, beeswax saponified with sodium bicarbonate, linseed oil potassium soap, beeswax and linseed oil potassium soap, and the eight Roman samples. Table 5 identifies the key components of beeswax and linseed oil soap.

Carbon dating results

Two samples of the Roman painting number 4 were submitted to Beta Analytic Laboratory for carbon-dating by accelerator mass spectrometry. One of the samples submitted was a portion of sample 4 in its original form, paint on lime mortar. The second was the dried aqueous extract collected after Soxhlet extraction. The results of these analyses were inconclusive, as neither sample yielded any measurable carbon upon combustion. This means that the organic content was very low, such that it could not be detected by the instrument, or that the acid pretreatment used would have affected the amount of the sample which remained for detection.

Experimental studies of wax paint media

Due to the small amount of organic compounds and their degree of deterioration, the characterization of the organic binding media in ancient paintings is a difficult task that often shows unreliable results. This is especially evident when trying to carry out a replica of an ancient painting by using the painting technique suggested at the conclusion of the chemical studies. It is not uncommon to observe that the physical characteristics of the original painting cannot be reproduced. In order to determine the capability of the beeswax-and-soap painting technique identified in this study to reproduce the characteristics of the ancient encaustic paintings, replicas of Roman wall paintings and Roman-Egyptian mummy portraits were executed with wax-and-soap encaustic paint.

Wax-and-soap wall paintings allowed the reproduction of complex large-scale murals without the need for *giornate* joints, as the painting was carried out on dry lime mortar, a feature consistent with the generalized absence of this type of joint in Roman wall paintings. Paint was easily applied, allowing the artist to reproduce both transparent and thick brushstrokes present in the original paintings. Unlike the fresco technique, wax-and-soap paint was able to reproduce the high color intensity of the Roman paintings. Pigments that degrade with lime – such as white and red lead, azurite, malachite, orpiment and red lake – were used without problems, calcium carbonate whites could be used as white pigment and impastos showed a smooth and greasy surface similar to Roman originals. Besides, the soap content in the medium allowed the artist to reproduce the crater formations occasionally seen in Roman thick brushstrokes

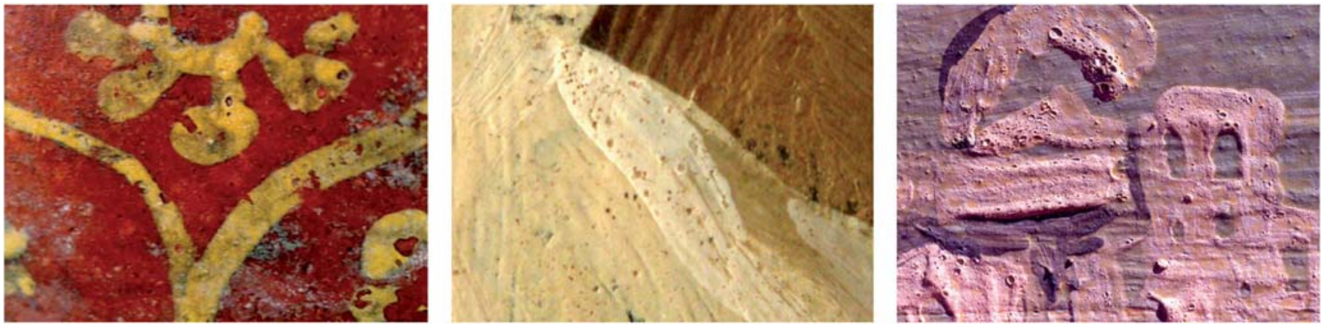

Fig. 4 Crater formations in the paint surface of a Roman wall painting from Villa dei Vetti, Pompeii, 62–69 AD (a), mummy portrait of a youth with a surgical cut in one eye, Egypt, 190–210 AD, encaustic on wood, The Metropolitan Museum of Art, New York (b), and wax-and soap encaustic on wood by José Cuní (c). Craters are often found in wax-and-soap encaustics due to the soap content in the binding medium.

Fig. 5 Current state of the first encaustic wall painting on lime mortar executed in modern times (José Cuní, 1962), showing no signs of decay in the painting. House in San Lorenzo del Escorial, Madrid.

(Fig. 4). Finally, wax-and-soap wall paintings carried out during the last fifty years in open porches and interior rooms showed high durability and lack of decay (Fig. 5).

Beeswax-and-soap paint applied at room temperature with a spatula allowed the artist to reproduce the thick strokes executed with a hard instrument shown in the faces of many mummy portraits, and application with a brush could accurately reproduce the long, thin, transparent or thick brushstrokes shown in eyes, jewels and garments of these portraits. As in Roman wall paintings, encaustic mummy portraits show crater formations that are typical of wax-and-soap paint due to its soap content (Fig. 4).

As mentioned above, paint made of beeswax saponified with an alkali does not allow the reproduction of neither mummy portraits nor Roman wall paintings due to its lack of cohesion.

Conclusion

The eight binding media extracts of Roman wall painting samples submitted showed strong evidence of the presence of beeswax and fatty acid soap through analysis by ATR FT-IR. Some absorption bands present in these extracts were not identified. In five of these samples the analysis by GC-MS detected all of the hydrocarbons and fatty acids determined from characterization of beeswax, and also detected a significant amount of unstaturated fatty acids, confirming the presence of beeswax detected by ATR FT-IR and suggesting that the paint medium also contained soap that could have been produced with drying oil. The results of testing the three remaining samples by GC-MS were inconclusive due to the very small size of the peaks, possibly caused by the low yield of the binding medium obtained by the aqueous extraction method used.

The ATR FT-IR analysis of a sample of an encaustic mummy portrait also showed strong evidence of the presence of beeswax and soap, together with some absorption bands that could not be identified. This is the first study that finds evidence through chemical analysis of the use of a common painting technique in Roman wall paintings and Egyptian mummy portraits. This unknown painting technique, unreported so far in the scientific literature,‡ would be based on beeswax and soap.

Egyptian mummy portraits are the best known examples of the ancient encaustic painting technique, whose composition remains subject to debate, as the two main theories about its composition – wax paint applied in molten state and wax saponified with an alkali – have not been confirmed by chemical studies and do not allow an accurate reproduction of paint strokes shown in some encaustic mummy portraits. The strong evidence of the use in an Egyptian mummy portrait of an encaustic paint made of beeswax and soap provides an alternative theory on the composition of an ancient water soluble encaustic paint. The support of this theory is not limited to the results obtained by chemical analyses; it also relies on experimental studies showing that wax-and-soap paint allows the artist to reproduce characteristic paint strokes in encaustic mummy portraits with great accuracy.

The alignment of the peaks characteristic of beeswax and soap shown by ATR FT-IR spectra of the eight Roman wall paintings and the mummy portrait analyzed strongly suggests that the Roman wall paintings analyzed were also executed with a water soluble encaustic made of beeswax and soap. These results agree with other studies of Roman wall paintings in Pompeii, Herculaneum, Marsala (Italy), Mérida and Complutum (Spain) which also identified the presence of beeswax and soap.

The use in Roman times of wax-and-soap encaustic in wall and easel paintings that are geographically and temporally distant (From Egypt to Spain from the 1st century BC to the 2nd century AD) suggests that this type of encaustic had a generalized use in Classical Antiquity. This widespread use strongly suggests that the water-soluble wax-and-soap encaustic paint identified in this study is a lost cold encaustic painting technique used by the Greco-Roman artists and whose reconstruction has been objective of artists and researchers during the last five centuries.[78]

As wax-and-soap encaustic is a painting technique unknown before the publication of this article, the identification of beeswax and soap in the binding medium of ancient paintings or polychrome objects suspected of being forgeries provides a strong argument in favor of their authenticity.

The results obtained from the chemical and experimental studies on Roman wall painting techniques performed in this study strongly suggest that the theory of the generalized use of the fresco painting technique in Roman wall paintings should be revised.

Further studies are necessary in order to broaden our knowledge on the composition of the wax-and-soap encaustic painting technique in antiquity, its variations according to local artists' schools, its geographical and temporal boundaries, its aging and degradation processes which would allow the development of conservation treatments for ancient paintings executed with this

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‡ With the exception of the article by J. Cuní and J. Cuní, *Archivo Español de Arqueología*, 1993.

technique, and its possibilities as a new painting technique for contemporary artists.

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