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Stratigraphic analysis of organic materials in wall painting samples using micro-FTIR attenuated total reflectance and a novel sample preparation technique

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Abstract Wall paintings typically contain low concentrations of organic materials within a largely inorganic matrix and are characterised by their high porosity and long-term exposure to severe environmental conditions. The identification of organic materials within specific paint or plaster layers is challenging and the inherent characteristics of wall painting samples present further complications. Embedding materials (such as epoxy, polyester and acrylic-based resins) used to produce cross-sections often infiltrate porous and leanly bound samples, and compromise the interpretation of Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra and the qualitative identification of natural organic materials. An alternative method for the preparation of cross-sections of wall painting samples was developed using cyclododecane ($C_{12}H_{24}$) as a temporary consolidant and barrier coating to encapsulate the sample, and to provide necessary support to produce a cross-section through microtoming. Impacts of traditional and novel sample preparation techniques on the identification of organic materials with micro-FTIR-ATR were examined for both replica and real wall painting samples.

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Introduction

Obtaining information on organic materials and more specifically on their distribution within the stratigraphy of a painting is crucial to clarify the original technology and subsequent physical history of the painting, to understand deterioration phenomena, to design appropriate diagnostic investigations, to undertake conservation interventions, and to assess the risk posed to original materials either by conservation treatments or by exposure to a particular environment. Wall paintings normally contain very low concentrations of organic materials within a largely inorganic matrix, and are commonly exposed to extreme environmental conditions and to a wide variety of deteriogens (light, liquid moisture, salts, microorganisms). As a result, organic materials often undergo significant chemical changes, further complicating their unequivocal identification.

One of the aims of the ongoing organic materials in wall painting (OMWP) project, coordinated by the Getty Conservation Institute [1, 2], is to evaluate the ability of various analytical techniques to identify the presence of natural organic materials within wall painting samples, differentiating between those which allow identification of their class (proteins, lipids, polysaccharides) and those which provide precise analysis (e.g. egg yolk, linseed oil, gum arabic). Among the invasive nondestructive analytical techniques carried out on cross-sections and which aimed to provide layer-specific information—staining tests, FTIR microscopy and Raman microscopy—few gave results illustrating their potential. One of the reasons for this overall trend is the unsuitability of traditional sample preparation

techniques for organic analysis on cross-sections of leanly bound and extremely porous samples.

The present paper briefly reviews some recent advances for spatially resolved FTIR analysis and outlines the issues related to paint sample preparation for stratigraphic organic analysis. The focus of the novel research is placed on the development and evaluation of an alternative sample preparation method which would better fulfil the criteria for analysis using micro-FTIR in attenuated total reflectance (ATR) on cross-sections of wall painting samples containing organic materials. The ability of this analytical technique to identify classes of organic materials within specific paint layers is examined through the comparison of results obtained on both replica and real wall painting samples prepared using traditional methods and the novel procedure described here. Advantages and limitations of micro-FTIR-ATR and of the developed sample preparation method are discussed.

Spatially resolved FTIR analysis of paint samples: recent advances

FTIR spectroscopy has long been employed for the analysis of painting samples [3, 4] and, when coupled with an infrared microscope, it can be a powerful technique for the stratigraphic analysis of both organic and inorganic components [5]. FTIR imaging analysis in reflectance and ATR mode, commonly used in the characterisation of industrial materials and pharmaceuticals [6–8], has been applied to the analysis of easel painting and wall painting samples [9–11]. Alternative energy sources such as synchrotron radiation (SR-FTIR) present significant advantages for the analysis of small areas on the surface of cross-sections owing to higher spatial resolution and improvement in S/N ratio compared with bench-top spectrometers. SR analysis in the field of cultural heritage science has become more common [12, 13], but the availability of SR is restricted and many laboratories require routine analysis of samples rather than access to research-level facilities.

FTIR microscopes equipped to perform analysis in ATR mode remain more commonly available and have been employed for the analysis of pigments [14], and of cross-sections of model and real wall painting samples [10, 11]. Micro-ATR is carried out by bringing an IR-transparent crystal into contact with the surface of a sample or cross-section. This is commonly achieved by raising the z-axis of a microscope stage until sufficient contact is made between the surface of the cross-section and that of the ATR objective. Due to attenuation of the IR radiation, and the total internal reflection which is provoked by the difference in the refractive indices between the crystal and the sample surface, an ATR spectrum is recorded from the area in direct contact with the crystal interface [15]. A particular

advantage of ATR is that it yields FTIR spectra which are similar to transmission standards, differing only in the lesser degree of penetration of radiation (and hence detection of bands) at longer wavenumbers. However damage of fragile surfaces can occur during analysis due to the pressure exerted by ATR crystals on samples [10]. Moreover, the size of ATR crystals is generally large (>50 μm) compared with the thickness of paint layers most often found in paintings. The positioning of the crystal on the sample is therefore particularly important, and requires a well-aligned microscope and precision in sample preparation. A variety of different crystals can be used for ATR analysis, and each crystal is associated with a different refractive index, hardness and IR window [16].

Sample preparation issues

The intrinsic characteristics of wall painting samples—the presence of materials of varied hardness, and the low concentration of organic binding materials relative to that of inorganic pigments and minerals—account for their overall porosity and brittleness, and for the difficulties often encountered in attempting to expose their stratigraphy. Traditional paint sample preparation methods [17, 18], deriving from the biomedical field, usually involve the use of synthetic embedding resins (polyesters, epoxies, acrylics). The function of an embedding material is twofold. First, it infiltrates porous samples and provides the necessary support to preserve their physical integrity during polishing or sectioning. Second, embedding allows the production of a block sufficiently large to orient a very small sample for microscopic analysis. Once embedded, samples are normally ground and polished using abrasive cloths. Microtoming, in which the sample is sliced under magnification using glass, metal or diamond blades, is also used to produce both cross-sections and thin sections of paint samples.

While such sample preparation procedures are well suited for inorganic analysis, traditional materials and methods do not fulfil the requirements for organic analysis on cross-sections. Interferences from polymeric embedding materials used to produce cross-sections have long been reported in conservation literature focusing on micro-FTIR [10, 19–21] and fluorochrome stain tests [19], and such issues are also encountered when using micro-Raman for organic analysis on cross-sections. Smearing of polymeric material over paint layers often occurs due to high surface tension and heat generated during polishing. Even very thin layers of synthetic resin over the paint cross-section may act as a physical barrier preventing chemical probes from accessing reactive sites, leading to false negative results with stain tests. Interpretation of FTIR spectra is also greatly hampered by the presence of embedding materials since many of their absorption bands

overlap with those of organic media commonly encountered as binders in paint or plaster layers (Fig. 1). Careful polishing using an appropriate sample holder and an aqueous dispersion of alumina nanograins has been shown to overcome this phenomenon and to greatly improve the analytical outcome of FTIR imaging and laser desorption mass spectrometry (LDMS) [21]. However, complete infiltration of porous and leanly bound samples (containing less than 20% binding medium) results in the presence of synthetic resin throughout the sample and no polishing or cutting procedures will succeed in producing a resin-free surface.

Several alternative sample preparation procedures have been developed in an effort to overcome the problems related to the infiltration of embedding resins. The use of various barrier coatings has been tested and some procedures proved satisfactory [19]. Preventing infiltration of embedding resins, however, results in loss of original materials during polishing or microtoming of porous, leanly bound samples (Fig. 2). IR-transparent materials such as potassium bromide or silver chloride have been used in the past for FTIR bulk analysis in transmission [20]. More recent developments using layers of compressed potassium bromide salts to sandwich a paint sample, subsequently polished to produce thin-sections [22] and cross-sections [11], allowed stratigraphic FTIR analysis to be carried out without interferences from the embedding material. As with barrier coatings, the absence of an infiltrating and consolidating medium strengthening porous samples may result in undesirable alterations and loss of the layered structure. The complete avoidance of embedding materials has also been investigated. Samples squeezed onto a diamond cell may retain their layer structure despite morphological alterations [22]. Ion cutting offers an elegant alternative but the availability of the technique precludes access for routine analysis [23].
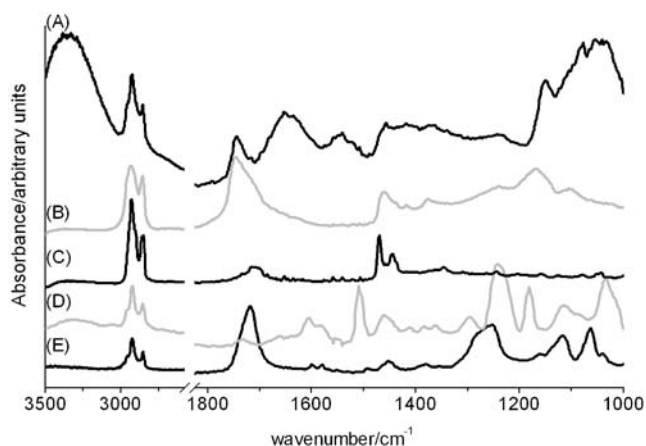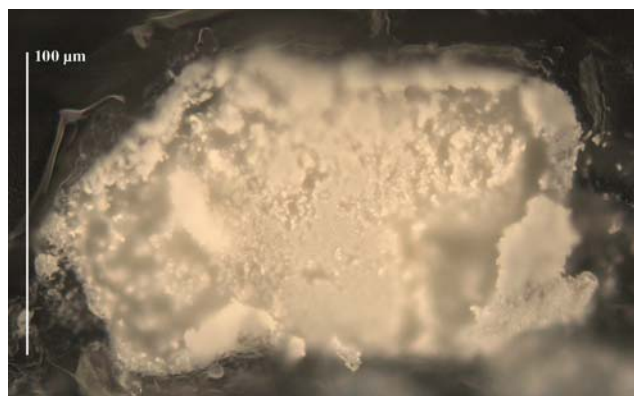

Fig. 2 Photomicrograph of a sample from the Getty reference archive containing lead white and less than 20% binding medium. Prior to embedding, the sample was coated with an acrylic emulsion thickened with fumed silica following the method described in [21]. Significant loss of original materials occurred during microtoming

Experimental

Samples

Both replicas and actual wall paintings were sampled. Six- to ten-year-old and naturally aged replicas from the Leonetto Tintori archive were selected for the OMWP project [1]. The availability of extensive documentation recording the pigments and binders that were applied on a fresh, partially set, and set lime-based plaster, and the relative proportions of binder and pigments, allowed the accurate evaluation of analysis performed with a wide range of techniques [1, 2]. FTIR-ATR spectra obtained from replicas containing lead white ($2PbCO_3 \cdot Pb(OH)_2$), calcium carbonate ($CaCO_3$), rabbit skin glue (protein) and linseed oil (ol18b) and lead white, calcium carbonate and rabbit skin glue (Az1b) are presented below. While technologically relevant, these replicas are nonetheless simplified models of real wall paintings.

Several samples were taken from historic wall paintings differing widely in terms of their materials, technologies, dates and geographical locations. The wall paintings in the Lotsawa temple in Nako, India, are an important example of twelfth-century Himalayan Buddhist art [24]. Extensive analyses were performed prior to the conservation of the eighteenth-century wall paintings in the church of Our Lady of Victory, Valletta, Malta, while the splendid wall paintings of Raunds, England, dating from circa 1400 retain an iconography unique in the UK.

Cross-section preparation methods

Traditional method

Some of the replica and real wall painting samples were prepared following traditional methods. The samples from Nako and Valletta were embedded in a polyester resin

Fig. 1 Micro FTIR spectra of *A* egg yolk and linseed oil (transmission), *B* linseed oil (transmission), *C* cyclododecane (ATR), *D* epoxy embedding medium (ATR) and *E* polyester embedding medium (ATR)

(Clear Casting Resin® Tiranti, London, UK), whereas that of the replica ol18b was embedded in an epoxy resin (Epofix®). All samples were manually dry-polished on Micro-mesh® cloths ranging from 1,000 to 12,000 mesh.

Alternative method

A sample from the replica Az1b and another taken from Raunds were prepared following an alternative procedure. The key element of the newly developed method is cyclododecane ($C_{12}H_{24}$), a commercially produced cyclic alkane which melts at 58 °C, dissolves in a range of non-polar solvents, and sublimates at room temperature. It has been used in the conservation field mainly as a temporary consolidant or hydrophobic barrier coating for aqueous treatments of water-sensitive works of art. The sublimation rate of cyclododecane has been shown to vary depending on ambient conditions (temperature, ventilation), on application methods and resulting thickness of the material and its depth of penetration, as well as on the porosity of the object [25–28]. A 0.08-mm film of melted cyclododecane applied on a glass slide was reported to sublimate within 24 h [26]. Sublimation of cyclododecane solutions (xylene and ShellSol 71) applied to saturate a limestone core sample (0.5-cm ∅ and 7-cm long) was shown to take 6–8 days [27].

The first step of the newly developed procedure consists in consolidating the porous sample with a saturated solution of cyclododecane in toluene (80% w/v) applied dropwise under vacuum, to allow maximum infiltration. The choice of solvent was found to have a significant impact on the efficiency of the consolidation and the resulting preservation of the physical integrity of the sample during microtoming. A network of needle-like crystals of cyclododecane is formed upon solvent evaporation. While fast-evaporating solvents produce a tightly packed network, which is said to be a better barrier coating, slow-evaporating solvents are usually recommended for consolidation purposes [25]. The following nonpolar solvents, characterised by different boiling points (b.p.), were evaluated for the purpose of sample consolidation: ShellSol 71 (b.p. 204 °C), Stoddard solvent (b.p. 149 °C), toluene (b.p. 111 °C), ethyl acetate (b.p. 77 °C) and petroleum ether (b.p. 35–60 °C). Samples containing a single lead white paint layer and low binding medium were consolidated under vacuum with saturated solutions of cyclododecane in the abovementioned solvents. Two samples were thus treated for each solvent/cyclododecane solution and mounted in acrylic resin. Subsequent microtoming to reveal cross-sections resulted in significant loss of the paint layer in all but the samples treated with cyclododecane/toluene solution.

The second step of the procedure consists in coating the sample with melted cyclododecane to ensure complete encapsulation and prevent resin infiltration. Using a small needle, the sample is swiftly moved across melted cyclododecane

heated on the edge of a glass slide. The waxy-looking coating surrounding the sample is observed under high magnification to assess its coherence, and excess material is removed using a microblade (Fig. 3). A light-cured acrylic resin (Technovit LC2000®) and a custom-made mould were used to produce resin blocks adapted to the working distance of the IR microscope and the shape required for efficient microtoming. After curing by exposure to blue light (440 nm), the bullet-shaped resin block is microtomed to reveal a cross-section of the sample. Two or three 10- to 20-μm-thick slices, from the top of the cross-section, are sacrificed to ensure the removal of the cyclododecane surface coating. The sample is then left for 24 h at room temperature and in a well-ventilated area. Complete sublimation of the cyclododecane coating, leaving a gap around the sample, is assessed by observation under high magnification before FTIR analysis.

Instruments

Diamond micro-ATR measurements were recorded using a Thermo Nicolet Nic-Plan IR microscope with a nitrogen-cooled MCT detector coupled to a Nicolet 560 IR Spectrometer. The Nic-Plan microscope is equipped with a ×15 Cassegrain objective for visual examination of samples using binocular eyepieces and a CCD camera. The contact area of the dedicated diamond micro-ATR objective is around 100-μm diameter. Spectra were recorded with 400 acquisitions at 4-cm^{-1} resolution over a spectral range of 4,000–650 cm^{-1} and no spectral corrections were applied.

An RMC MT-7 microtome, equipped with a glass knife fixed on a rotary stage, was used to produce cross-sections of the samples prepared following the alternative procedure. The glass knife stage was manually moved in 10- to 20-μm increments between each cutting. The movable arm and sample holder containing the bullet-shaped resin block was
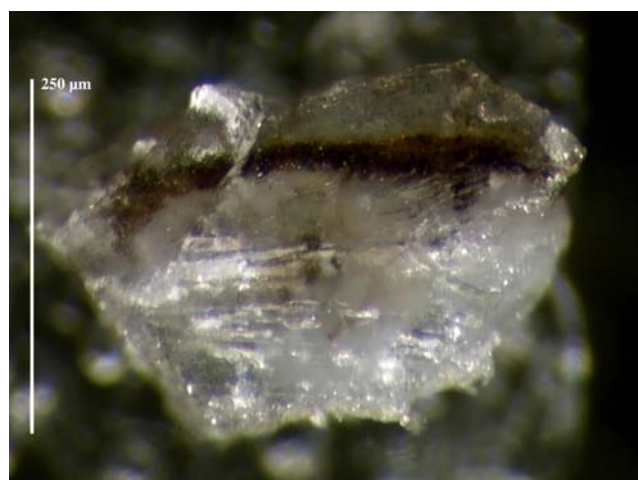

Fig. 3 Sample from a Tintori wall painting replica after preconsolidation with cyclododecane solution and coating with melted cyclododecane

manually lowered towards the glass knife. The apparatus includes binoculars allowing examination under magnification while cutting the resin block.

Results and discussion

Impact of traditional sample preparation technique on FTIR-ATR analysis

Nako, India

The area of the sample analysed consists of a thick preparation layer (approximately 250 μm) containing IR-inactive vermilion (HgS), realgar (AsS) and orpiment (As_2S_3), and large quantities of calcium carbonate (Fig. 4a–c). The FTIR-ATR spectrum illustrates the presence of the polyester embedding material, with strong absorption bands at $1,718$ cm^{-1} and around $1,300$–$1,000$ cm^{-1} corresponding to C–O stretching vibrations. However, small absorption bands at $1,650$ cm^{-1} and $1,550$ cm^{-1} could be ascribed to amide I and amide II carbonyl stretching, suggesting the presence of a proteinaceous material (Fig. 4d). By comparison, no signal can be assigned to original organic materials in the reflectance spectrum due to the overwhelming *restrahlen* distortion of the C–O stretching from calcium carbonate at approximately $1,400$ cm^{-1}. GC-MS analysis of the painted ceiling of the Lotsawa temple indicated the presence of collagen-based glue [29].

Our Lady of Victory, Valletta, Malta

Scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX) of a cross-section taken from the blue robe of the Virgin revealed the presence of four paint layers (Fig. 5a–c). Layer 1 is composed of calcium carbonate, the main component of the limestone support; layer 2 presents finely ground black particles in a lead white matrix; layer 3 is composed of ultramarine ($Na_{6-10}Al_6\ Si_6O_24S_2$); and layer 4 shows the presence of a varnish layer. The fluorescence of
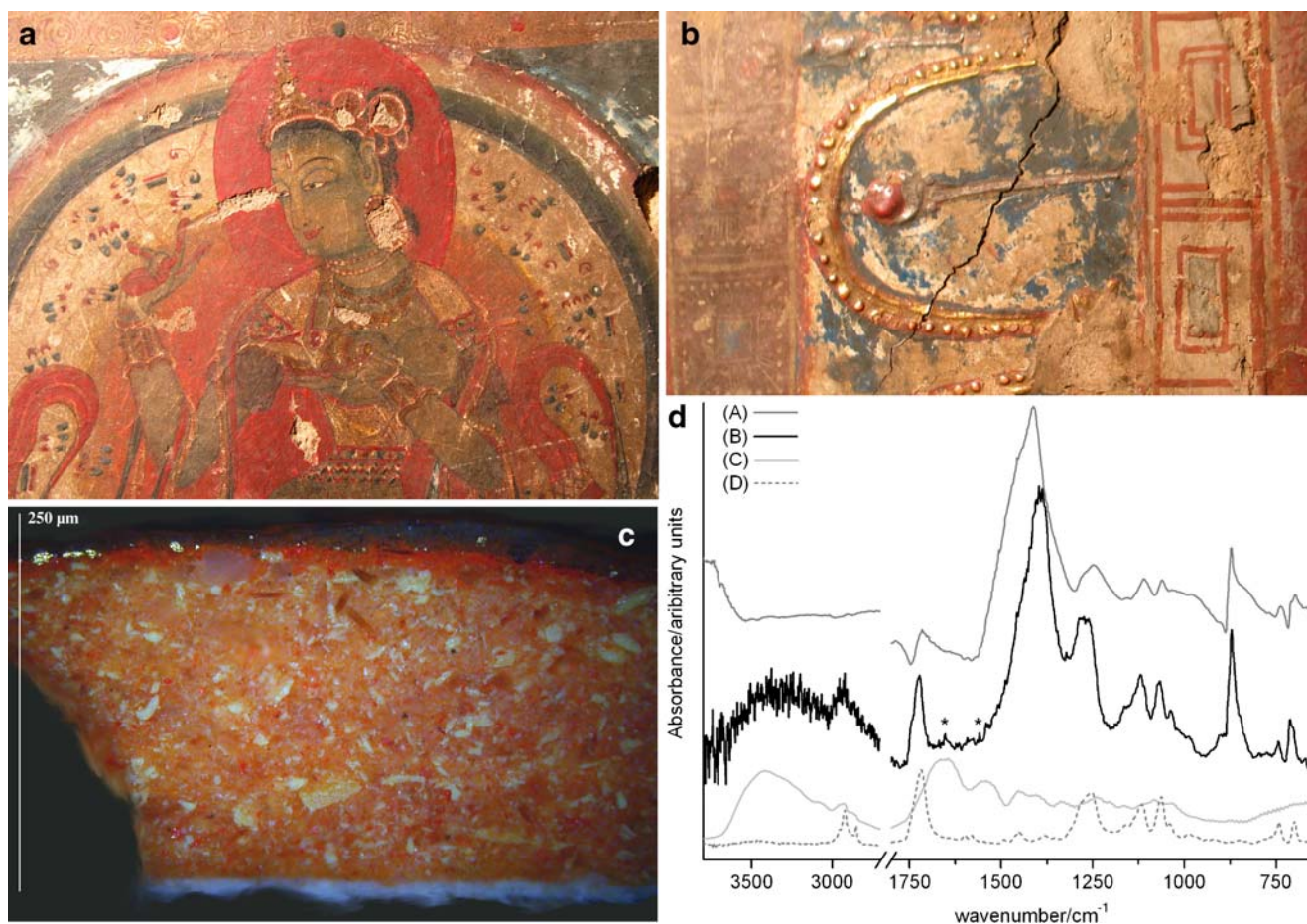

Fig. 4 **a** General view of the twelfth-century wall painting in Lotsawa temple, Nako, India. **b** Detailed view showing gilded relief from which a sample was taken. **c** Photomicrograph of the cross-section (original magnification ×200). **d** Micro-FTIR spectra: *A* reflectance spectrum recorded from an area approximately 100×100 μm on the preparation layer below the thin layer of gold, *B* ATR spectrum recorded from the same area, *C* rabbit skin glue FTIR transmission reference and *D* polyester embedding medium (ATR)
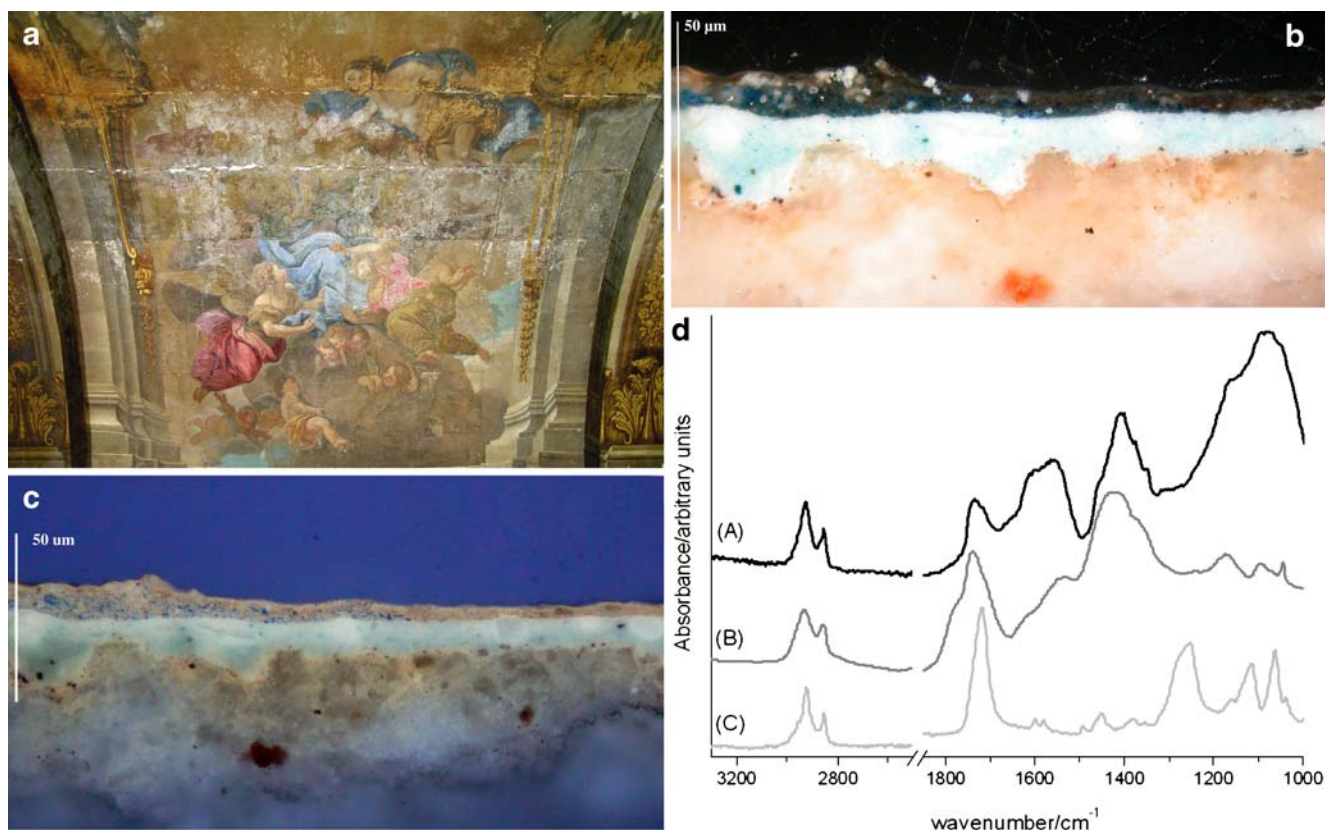
Fig. 5 **a** General view of the eighteenth-century wall painting in Valletta, Malta. **b** Photomicrograph of the cross-section from a sample of the Virgin's robe (original magnification ×100). **c** Photomicrograph of the same sample under ultraviolet illumination. **d** Micro-FTIR spectra: *A* ATR spectrum recorded from an area approximately 100× 100 μm including the lead-based and ultramarine paint layers, *B* linseed oil and lead white FTIR transmission reference and *C* polyester embedding medium (ATR)

the upper section of layer 1 as well as of layers 3 and 4, under ultraviolet illumination, indicates the presence of organic materials. The FTIR-ATR spectrum shows the characteristic absorption band of ultramarine around 1,100–1,000 cm^{-1} and is comparable to that of lead white in linseed oil (transmission reference), but the interference with bands ascribed to the polyester embedding medium precludes reliable binding medium identification (Fig. 5d). The presence of linseed oil in the paint layer and as a component of the nonoriginal varnish was later ascertained by pyrolyis-GC-MS analysis.

Tintori replica ol18b

Interferences resulting from the presence of embedding materials on the surface of the cross-section are obvious, especially between 1,300 and 1,000 cm^{-1} (Fig. 6). The presence of a carbonyl stretching band around 1,750 cm^{-1} can be ascribed to the presence of lipids in the linseed oil. However, the absorption bands at 1,660 cm^{-1} and 1,560 cm^{-1} cannot be attributed with certainty to the presence of proteins due to possible overlapping bands from the epoxy embedding medium.

Impact of alternative sample preparation technique on FTIR-ATR analysis

Tintori replica Az1b

Examination of samples under bright field illumination with a light microscope provides evidence of the effects of preparation procedures. While a thin film of polymeric material covers the sample prepared using traditional materials and methods (Fig. 7a), it is absent from that prepared with the cyclododecane/microtoming procedure (Fig. 7b). FTIR-ATR measurements were collected along with transmission (diamond cell) measurements obtained from a powdered portion of the sample for comparison. Both the transmission and ATR spectra are similar, presenting N–H stretching bands around 3,200 cm^{-1} and C–H stretching bands around 2,800–3,000 cm^{-1}, while the amide I band around 1,650 cm^{-1} is more apparent in the ATR spectrum than in that from transmission (Fig. 7c). While absorption bands around 3,000–2,800 cm^{-1} (C–H stretching) could be ascribed to the cyclododecane, the reduced intensity of C–H stretching bands and the absence of absorption bands around 1,715–1,700 cm^{-1}, which are characteristic of cyclododecane,
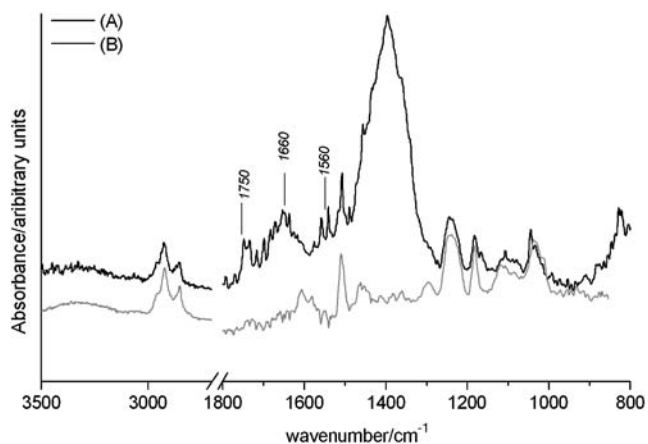
Fig. 6 Micro-FTIR-ATR spectra of *A* Tintori sample ol18b with absorption bands indicating the possible presence of proteinaceous materials marked and *B* epoxy embedding medium

exclude interferences which could be attributed to the presence of the cyclic alkane (Fig. 7c). Similarly, the presence of acrylic resin within or over the sample is unlikely considering the lack of absorption bands characteristic of the embedding medium (e.g. 1,729 cm^{-1}, 1,241 cm^{-1}, 1,151 cm^{-1}). The exclusion of embedding materials therefore facilitates the interpretation of the ATR spectrum and the identification of the organic component (proteins).

Raunds, UK

The appearance of the cross-sections prepared following the traditional and alternative methods differs greatly (Fig. 8a–c). ATR measurements were recorded from a sample prepared following the cyclododecane/microtoming procedure. The area first analysed overlapped both ground layers (Fig. 8c). Absorption bands indicate the presence of both calcium carbonate with C–O stretching in the 1,400–1,500 cm^{-1} region and C–O bending in the 880–860 cm^{-1} region, and calcium sulfate (CaSO$_4$) with S–O stretching in the 1,140–1,080 cm^{-1} region and O–H stretching in the 3,550–3,400 cm^{-1} region (Fig. 8d). Weak C–H stretching bands are observable around 3,000–2,800 cm^{-1} and could indicate the presence of organic materials rather than that of cyclododecane considering the absence of other absorption bands characteristic of the cyclic alkane. The presence of an amide I carbonyl stretching band around 1,650 cm^{-1}, which would indicate proteins, is difficult to ascertain due to the O–H bending of gypsum (CaSO$_4$·2H$_2$O) around 1,620 cm^{-1}. ATR analysis was performed on each ground layer using a movable knife-edge aperture device to isolate the area of analysis. The spectra are very noisy due to the dimension of the area analysed (20×20 μm) and the extreme porosity of the layers under investigation. The S–O stretching around 1,100–1,200 cm^{-1}, characteristic of gypsum, is only visible in the spectrum acquired on the upper ground, while absorp-
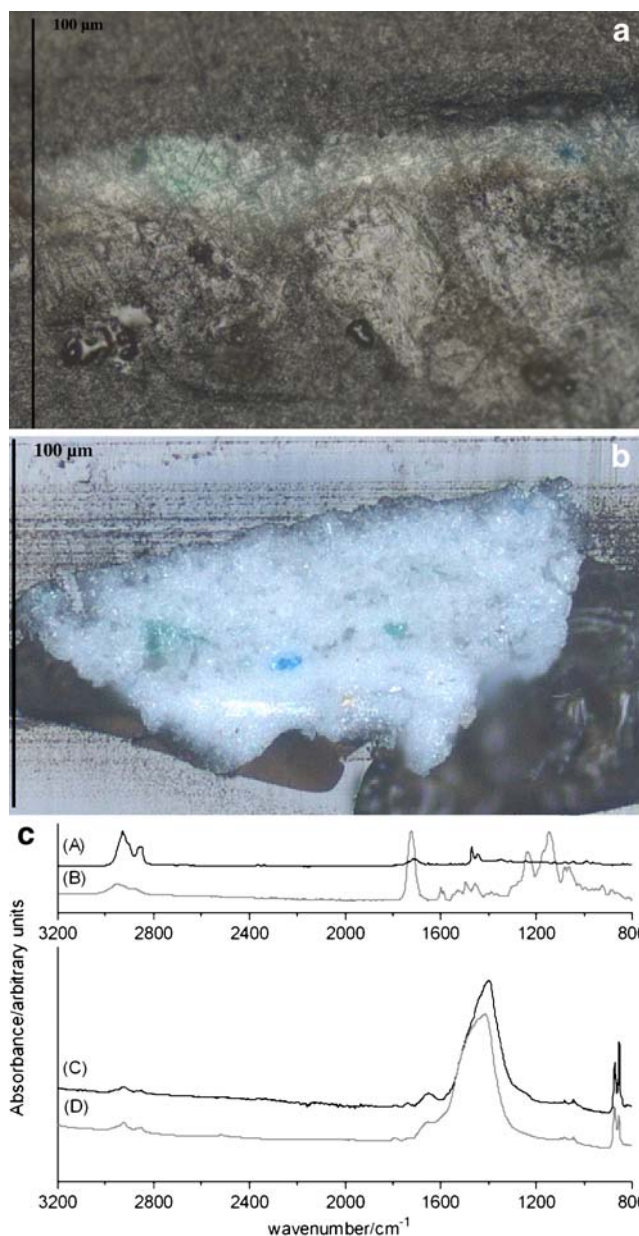

Fig. 7 a Tintori sample Az1b embedded in Technovit® and polished on Micro-mesh® cloths. Photomicrograph captured under bright field illumination (original magnification ×200). **b** Cross-section of the same sample prepared following the newly developed procedure; photomicrograph captured under bright field illumination. **c** Micro-FTIR spectra of *A* cyclododecane (ATR), *B* Technovit® embedding medium (ATR), *C* sample Az1b (ATR) and *D* sample Az1b (diamond cell transmission)

tion bands of calcium carbonate are visible in both spectra (Fig. 8e). These results indicate a mixture of calcium carbonate and gypsum for the upper ground and only calcium carbonate in the lower ground. Once again, the presence of embedding materials within or over the sample is unlikely. While the presence of organic materials is suspected, absorption bands from original inorganic components preclude firm conclusions regarding the nature of the binding medium within the ground layers.
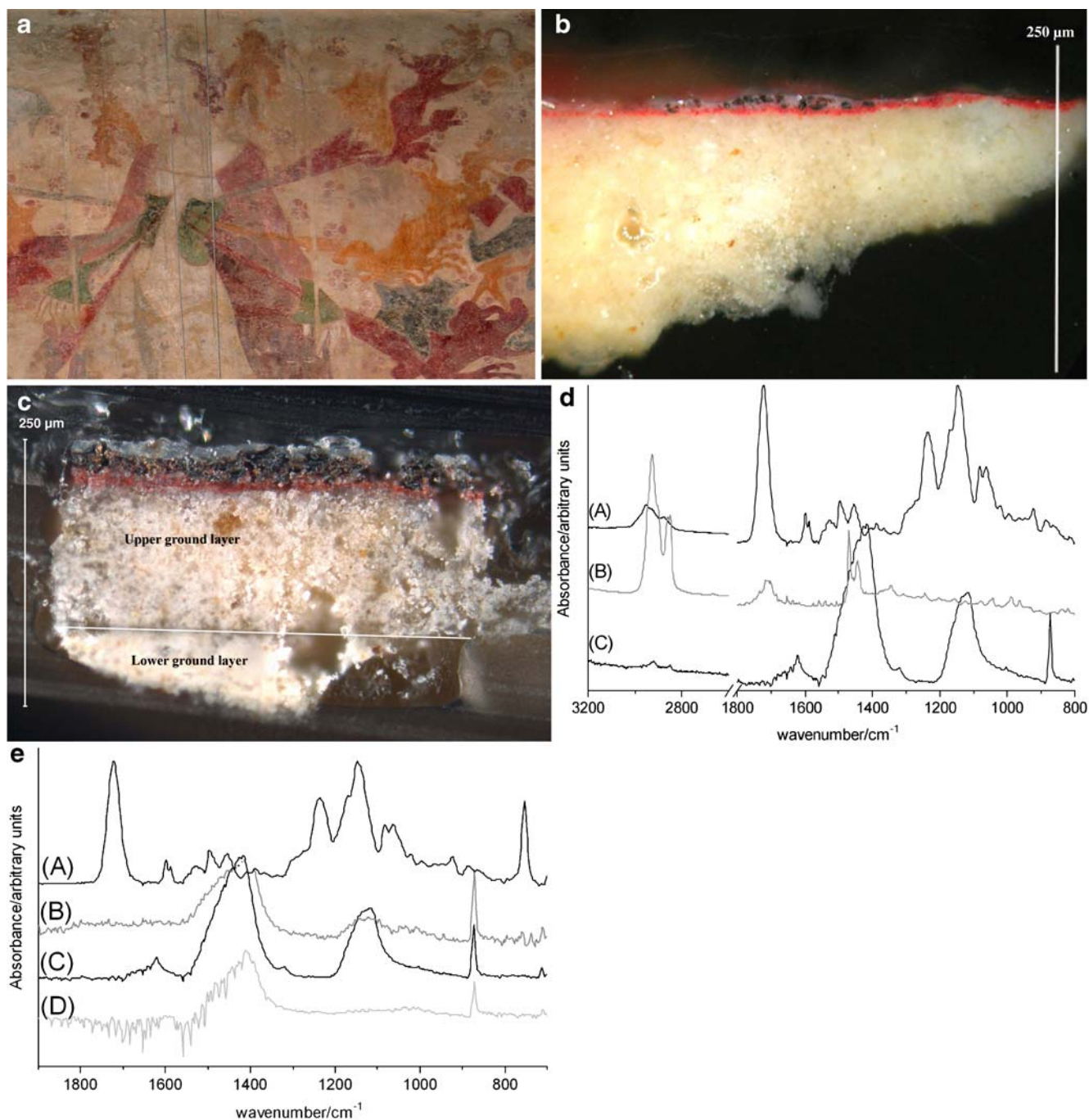
Fig. 8 a General view of the fifteenth-century wall painting in Raunds. **b** Photomicrograph of a cross-section prepared following traditional procedure and captured under dark field illumination (original magnification ×200). **c** Cross-section of a similar sample prepared following newly developed procedure and captured under dark field illumination (original magnification ×200). **d** Micro-FTIR-ATR spectra of *A* Technovit®, *B* cyclododecane, *C* area of the sample including both ground layers. **e** Micro-FTIR-ATR spectra of *A* Technovit®, *B* upper ground layer, *C* area including both ground layer and *D* bottom ground layer

Conclusions

FTIR spectroscopy can rarely provide information on the exact nature of the organic materials present within the complex mixtures which usually characterise paint layers, though analysis from FTIR can be used to elucidate their main classes. Among spectroscopic analytical techniques, micro-FTIR-ATR presents several advantages: it is fairly accessible and provides layer-specific data on both organic and inorganic materials, although the absorption bands of inorganic materials commonly present in paint layers (especially calcium carbonate, lead carbonates, calcium sulfate

and calcium oxalates) often overlap those of organic binding media. Significant complications in the interpretation of FTIR results may occur for samples from wall paintings treated with synthetic conservation materials. ATR spectra are also easily compared with transmission spectra recorded in reference databases (for example http://www.irug.org). The specifications of the equipment used for this research precluded analysis of extremely thin paint layers due to the diameter of the diamond crystal, though smaller crystals are now available. However, the placement of the crystal on the surface of cross-sections remains an issue for a variety of reasons which include the precision of the alignment of the microscope, and potential damage of samples as a result of the pressure exerted by the crystal during analysis. Finally, the nondestructive nature of the analysis allows further investigations on the cross-section.

Sample preparation protocols for organic analysis on cross-sections have been given comparatively less attention than for bulk analysis. Although traditional procedures might not present significant drawbacks for nonporous samples containing high concentrations of organic materials, the occurrence of synthetic resins within leanly bound porous wall painting samples often precludes reliable characterisation of binding media. The procedure developed involving the use of cyclododecane and microtoming has drawbacks: it requires significant sample manipulation and dexterity, after sublimation of cyclododecane the stability of the sample within the resin block may be reduced, and it does not lead to photogenic stratigraphies compared with traditional sample preparation methods. However, it does present the advantage of limiting interferences from embedding materials which might compromise the interpretation of FTIR-ATR spectra. The low binding media content of both samples prepared following the novel procedure is illustrated by the reduced intensity of the C–H stretching and amide I bands. In such case the exclusion of embedding material is of paramount importance and allowed unequivocal identification of the presence of organic materials—in the case of Raunds—and the class of the organic material (i.e. proteins) for the replica sample. No interference from either the cyclododecane, which appears to have sublimated after 24 h, or the acrylic resin was noted. Although barrier coatings have been previously used for paint samples, the novel consolidation method significantly contributes to the preservation of the physical integrity of the sample thus optimising the possibility of acquiring layer-specific data. Such cross-section preparation procedure is not suitable for all samples, especially those containing coarse pigment particles or fillers, and it requires further testing in order to fully establish its limitations. However, initial results show significant advantages for micro-FTIR-ATR analysis and could provide a novel means for micro-Raman analysis of cross-sections, where tradi-tional embedding materials give rise to strong luminescence backgrounds.

References

1. Pique F (2007) A methodology for the identification of organic materials in wall paintings. In: Drdácký M, Chapuis M (eds) Safeguarded cultural heritage: understanding and viability for the enlarged Europe. Proceedings of the 7th European conference SAUVEUR, 31 May–3 June 2006, Prague, Czech Republic
2. Getty Conservation Institute (2008) Organic materials in wall paintings (OMWP) project. http://www.getty.edu/conservation/science/omwp/index.html. Accessed 8 April 2008
3. Derrick MR, Stulik D, Landry JM (1999) Infrared spectroscopy in conservation science. Getty Conservation Institute, Los Angeles
4. Casadio F, Toniolo L (2001) J Cult Herit 2:71–78
5. Schulz H, Kropp B (1993) Fresenius J Anal Chem 346:114–122
6. Chalmers JM, Everall NJ, Hewitson K, Chesters MA, Pearson M, Grady A, Ruzicka B (1998) Analyst 123:579–586
7. Chan K, Kazarian S (2007) Appl Spectrosc 61:48–54
8. Ricci C, Eliasson C, Macleod N, Newton P, Matousek P, Kazarian S (2007) Anal Bioanal Chem 389:1525–1532
9. van der Weerd J, Brammer H, Boon JJ, Heeren RMA (2002) Appl Spectrosc 56:275–283
10. Nevin A (2005) Z Kunsttechnol Konservierung 19:356–368
11. Mazzeo R, Joseph E, Prati S, Millemaggi A (2007) Anal Chim Acta 599:107–117
12. Salvado N, But S, Tobin MJ, Pantos E, Prag A, Pradell T (2005) Anal Chem 77:3444–3451
13. Cotte M, Checroun E, Susini J, Walter P (2007) Appl Phys A 89:841–848
14. Marengo E, Liparota M, Robotti E, Bobba M (2005) Anal Chim Acta 553:111–122
15. Hind AR, Bhargava SK, McKinnon A (2001) Adv Colloid Interface Sci 93:91–114
16. Sudo E, Esaki Y, Sugiura M, Murase A (2007) Appl Spectrosc 61:269–275
17. Khandekar N (2003) Rev Conserv 4:52–64
18. Wachowiak M (2004) JAIC 43(3):205–226
19. Derrick M, Souza L, Kieslich T, Florsheim H, Stulik D (1994) JAIC 33:227–247

20. Pilc J, White R (1995) Natl Gallery Tech Bull 16:73–84
21. Wyplosz N, Koper R, van der Weerd J, Heeren R, Boon J (2000) In: Art et Chimie, la couleur. CNRS, Paris
22. van der Weerd J, Heeren RMA, Boon JJ (2004) Stud Conserv 49:193–210
23. Boon J, Asahina S (2006) Microsc Microanal 12:1322–1323
24. Bogin S (2005) Z Kunsttechnol Konservierung 19:199–230
25. Jäegers E, Jäegers E (1999) Brit Mus Occas Pap 135:37–42
26. Brückle I, Thornton J, Nichols K, Strickler G (1999) JAIC 38:162–175
27. Stein R, Kimmel J, Marincola M, Klemm F (2000) JAIC 39:355–369
28. Muros V, Hirx J (2004) JAIC 43:75–89
29. Pitthard V, Griesser M, Stanek S, Bayerova T (2006) Macromol Symp 238:37–45