Accepted Manuscript

Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from art-works

Victòria Beltran, Nati Salvadó, Salvador Butí, Gianfelice Cinque

PII: S0026-265X(14)00177-5
DOI: doi: [10.1016/j.microc.2014.09.001](https://doi.org/10.1016/j.microc.2014.09.001)
Reference: MICROC 2029

To appear in: *Microchemical Journal*

Received date: 5 June 2014
Revised date: 30 July 2014
Accepted date: 3 September 2014

Please cite this article as: Victòria Beltran, Nati Salvadó, Salvador Butí, Gianfelice Cinque, Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from art-works, *Microchemical Journal* (2014), doi: [10.1016/j.microc.2014.09.001](https://doi.org/10.1016/j.microc.2014.09.001)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from art-works

Victòria Beltran¹, Nati Salvadó^{1*}, Salvador Butí¹, Gianfelice Cinque²

1. *Dpt. d'Enginyeria Química. EPSEVG. Universitat Politècnica de Catalunya, Av. Víctor Balaguer s/n, 08800 Vilanova i la Geltrú, Barcelona*

2. *Diamond Light Source, Harwell Campus, Chilton-Didcot OX11 0DE Oxon, U.K.*

* Corresponding author:

E-mail address: nativitat.salvado@upc.edu

Telephone: 0034938967717

Fax: 0034938967700

ABSTRACT

The presence of coating on manufactures either to protect them from the environment, or to give them specific properties - as well as simply to change their aspect - has shown to be a constant practise throughout history. Their characterization is complex not only because of the inherent variability and diversity of the composition, but also due to the small amount of sample material available. A methodology to study those coatings using microFTIR is proposed. In some cases the use of microSR-FTIR which heavily increases spatial resolution particularly appropriate for the analysis of these heterogeneous samples is also proposed. Data processing tools such as distribution maps of specific infrared bands and curve fitting facilitate the interpretation of the spectra and help identifying heavily overlapped spectra. Through the identification of individual bands, it has been possible to discriminate materials and comprehend the interaction processes during aging. Infrared spectra from reference aged materials of known production dates and which are essential in understanding those processes are given. A set of selected case studies including materials of different chemical nature and various historical periods are presented: identification of guanine on an inner coating of a hope chest; determination of a protein glue coating from a gilded Baroque altarpiece; assessment of a beeswax superficial application during an historical restoration of a late 19th century canvas painting; identification of impurities of shellac wax in a shellac coating on a wood moulding from a medieval altarpiece; aging and reaction compounds in *Pinus* resin, drying oil and green copper pigment mixtures used as colour coatings on Baroque and modern desks.

Keywords: microFTIR, Synchrotron Radiation, vibrational microspectroscopy, coatings, varnish, cultural heritage, guanine, colophony, wax, protein.

1. Introduction

The application of organic coatings on historic manufactures either to protect them from the environment or to give them specific properties - as well as simply to change their aspect - has been a constant practise throughout history [1].

The materials used for the purpose are very diverse in nature, depending on what the covering was intended for, the availability of the materials, the easeness of application, or simply the fashion in the historic period [2].

Being at the surface, such covering layers are often totally/partially lost depending on the material properties, and frequently appear substituted by modern materials. Their characterization is in general complex not only because of the inherent variability and diversity of the substances present, but also due to the small amount of sample material available, generally a micrometric layer (between 5-10 μm), often modified by subsequent restorations [3].

As in other studies related to cultural heritage materials, the aging and alteration of the original materials, that is, the chemical reactions occurring with atmospheric pollutants and among the substances - contemporaneous or not to the piece under study - must be taken into account. This implies that the reference materials we have access to can hardly correspond to the historic materials, as they reached us.

The knowledge of the nature of these materials is, however, of great interest for a number of reasons; first, the historical insight obtained about the techniques used in the manufacture of the objects: the making of, including processing from centre of production to finished artwork, their relationship to contemporary artists or workshops, and the identification of the natural sources. Secondly, elucidating the conservation conditions in order to plan, if necessary, the optimal restoration strategy.

The availability of standardized and increasingly faster infrared (IR) equipment together with the intrinsic high sensitivity of the absorption set-up in the mid-infrared spectral range have made of IR one of the most widely used techniques for the characterisation of cultural heritage materials [4]. The principal advantages are related to the small quantity of sample needed, the easeness of identification of very diverse materials, the speed at which results can be obtained via IR fingerprinting, the low cost of analysis and the non destructiveness character of the technique.

The coupling of IR spectroscopy to a microscope extends its capabilities into the microanalytical range, providing the spatial resolution necessary for the identification of submillimetric structures/particles. It is more and more common to find infrared microscopes in laboratories dedicated to the microanalysis of cultural heritage materials. Adequate selection of the samples for analysis is especially challenging given the small quantity of material available from the historic objects [5,6].

Fourier Transform InfraRed (FTIR) spectrometry is the standard lab method which provides easy spectral information and identification of the coating materials when a

reference database is available [7-9]. The main object of this article is to demonstrate the advantage of this technique for the identification of those coatings over more precise or costly and lengthy techniques such as GC-MS [10]. Nevertheless, when those techniques are needed, the information that is available from FTIR microanalysis (μ FTIR) has been shown to be always a key in the characterization process and its optimization [11].

Another objects of this research is to investigate the spectral and spatial features across the submillimetric historic surface layer, identifying the spatial distribution of the chemical substances. For this reason Synchrotron Radiation FTIR microspectroscopy (μ SR-FTIR) was used to obtain the necessary spectral quality - high signal-to-noise ratio - at the maximum IR magnification available - 36x - for an improved minimum detection limit and reliable interpretation of the spectra with few microns spatial resolution [5, 12]. This goes beyond the limits of spectral interpretation by conventional IR techniques and is vital for the study of historical samples.

Many types of coating materials have been used over time. They can be essentially classified into five main groups: waxes, oils, gums, resins and protein materials [13]. The resins used are secretions of animal or vegetal origin, which can be chemically differentiated into several large families; sesquiterpenoids (shellac), triterpenoids (mastic, elemi and dammar), diterpenoids based in the communic acid (sandrac, amber and copal) and diterpenoids based in the abietic acid (colophony and turpentine) [13]. However, we sometimes find unexpected substances which presence must be accounted for.

A methodology for the analysis of the coatings using μ FTIR is herewith proposed that permits to obtain definitive results, or at least to delimit the analysis features in an easier and more focused way. With the advantage of being non-destructive, the same sample preparation may be reused. Various examples corresponding to materials of a different chemical nature, applied with different purposes and at different historical periods are shown.

2. Materials and methods

2.1 Reference samples

A set of reference materials has been collected, selected and naturally aged from different restoration workshops, dry goods shops and commercial products and of natural origin from the author's own collection. In addition, naturally aged *Pinaceae* resin materials (about two centuries) were supplied by "Economic Botany Collection of the Royal Botanic Gardens, Kew", in Richmond (Greater London - UK). Moreover, a resin from the 14th century was obtained from a knot of a dated coffered ceiling made of *Pinus* wood. Finally, copper abietate was synthesized following the method from L. Steele [14] using abietic acid (Fluka Analytical ref. 101392305) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Panreac ref. 131270.1211).

2.2 Historic coatings

Historic coating samples, a few hundred micrometres in size, extracted from several artworks have been analysed. The samples were obtained from: an 16th century hope chest (MADB9909 reference number), an early 20th century writing desk (MADB71747 reference number) and a writing desk from the last quarter of the 17th century (MADB64160 reference number) all them belonging to the Museu del Disseny de Barcelona [15]. Some other samples were obtained from a Baroque altarpiece dedicated to Santa Càndia from the Cathedral of Santa Maria de Tortosa (Catalonia); a canvas entitled *View of the Barcelona Port* (2,18 m x 7,30 m in size) by Francesc Soler i Rovirosa, painted in 1889 from the Museu Marítim de Barcelona [16]; a gothic altarpiece dedicated to Our Lady, by Pasqual Ortoneda, on display at the Museum Vinseum (Vilafranca del Penedès, Catalonia); and a polychrome wood coffered ceiling in the 14th century from Santa Maria de Paretdelgada Chapel (La Selva del Camp, Catalonia).

2.3 Analytical instrumentation and methods

2.3.1 Microscopic observations (OM)

The microsamples were observed, handled and fragments selected for analysis with a Stereomicroscope, SMZ800 Nikon. Flat sites from selected fragments were observed with an Optical microscope Eclipse LV100 Nikon under visible and UV light.

2.3.2 Scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDS)

Scanning Electron Microscopy (SEM), JEOL-5600, with elemental analysis using the PCXA LINK EDS microanalyzer are used in order to obtain information of the composition and thickness of the layers of the samples. Small fragments were carbon coated to ensure the electrical conductivity.

2.3.3 Infrared spectroscopy

Selected fragments were analysed using mid infrared microspectroscopy, μ FTIR. The measurements were taken in transmission mode using an AIM-8800 microscope with an MCT detector coupled to the Shimadzu IRAffinity-1 FTIR spectrometer. A transmission spectrum requires a flat sample with an adequate thickness. For this, selected fragments were squeezed between two diamonds into an anvil cell. The spectra were taken from one of the diamonds and a spot of 100x100 and 40x40 square micrometres surface area was analysed. This procedure helps the separation of the different compounds present. The measurement interval was 4000-700 cm^{-1} with a resolution of 4 cm^{-1} and 256 scans.

Synchrotron-based infrared microspectroscopy (μ SR-FTIR) measurements were taken at beamline MIRIAM B22 of the Diamond Light Source [17]. Two Bruker 80 V Fourier Transform IR Interferometers are equipped with Hyperion 3000 microscope, and broad-band and high sensitivity MCT detectors. The spectra were obtained in transmission mode from a sample dispersed on a diamond window following the same compression cell preparation method described above, using a small beamspot of 12x12 square microns, 4 cm^{-1} resolution, co-adding 256 scan at scanner velocity 80 kHz (35 sec), in the 4000 to 650 cm^{-1} or 500 cm^{-1} wavenumber range. IR maps of the molecular composition were obtained by scanning the sample via a micrometric resolution motorized X-Y stage.

An accurate analysis of the spectrum is able to resolve overlapped bands [18]; When has been needed overlapped bands have been processed using the curve fitting software from OPUS 7.2. First, the spectra have been baseline corrected then the band positions have been found from the second derivative of the curve and finally, the spectrum is fitted by a set of Lorentzian curves. The method is applied to fit all the bands appearing only the significant ones are shown.

3. Results and discussion

3.1 Guanine, unexpected coating

The first example corresponds to the coating material from the interior of a hope chest dated from 16th century by historians, obtained during the process of restoration.

The very thin coating layer is directly applied onto the wood; the sample was mechanically extracted under the stereomicroscope to help choosing the most representative areas which were measured with μ FTIR. The material was fragile, translucent and uncoloured, **Fig. 1a**.

Two different materials have been identified; anhydrous guanine [19] and a protein substance shown in **Fig. 1b,c** respectively. Guanine is a material used in pigment production to obtain a nacreous (pearlescent) effect, a natural pearl essence pigment as well as, to make synthetic pearls and cosmetic products.

Guanine appears as small crystallites of elongated shape, about 10-40 microns length and 40-50 microns thickness; it has a low density 1.6 g/cm³, is stable to the light, brilliant/iridescent, and has a refraction index of 1.85 [20]. It is a typical interference pigment showing a white pearlescent effect. Guanine is obtained from white fish scales. The composition is 75-97% guanine and 3-25% hypoxanthine, the ratio depends on the fish species [21,22]. The guanine (C₅H₅N₅O) is a nucleic acid in particular a purine base. From the historical point of view guanine is first reported in 1656 by François Jacquin (a rosary maker from Paris) who isolated it from a fish scale suspension [22]. The infrared spectrum obtained from the sample is very similar to the reference spectrum from the literature. Assigning the absorption bands to specific vibrations is complex [19]. R. Pedro Lopes *et al.* propose that the 1672 and 1697 cm⁻¹ bands (**Fig. 1c**) are due to ν (C=O) coupled to the NH₂ scissoring and (N1)H in-plane bending vibrations [19].

Finally, the protein substance determined may also be related to the fish or to the glue used to stick together the pigment particles.

This is an example of how the identification of the materials can be obtained from an extremely small sample with minimal preparation and manipulation. The coating used in this case, guanine, is a substance which has never been described or found in artworks and thus was wholly unexpected.

3.2 Reducing the brilliance of a gold foil

The coatings applied over the gold foils from a Baroque altarpiece of the 17th century placed in the Cathedral Santa Maria in Tortosa, which, when the samples were extracted, was in process of restoration, are studied. In this period the altarpieces were extensively gilded [23]. The gold foil was applied over a bole (in general a red or yellow clay). The bole provides a certain amount of plasticity facilitating the application of metallic foil. Several finishings were given to obtain a specific colour and/or shine. In order to maximize brightness and to give the illusion of solid gold, the surface was polished. Sometimes, however, on certain parts of the altarpiece, a tarnish or colour finishing was desired and thus, it was necessary to apply a coating [24]. However, distinguishing among dirt deposited or a chromatic coating layer is sometimes difficult and at the same time very important for the adequate restoration respecting the original purpose. In **Fig. 2a,b** a thin coating layer (<2 μm) covering the whole gold surface is seen. The analysis by SEM-EDS indicates the presence of Ca, Si and S. A small fragment of this superficial layer was mechanically separated. Three samples from different points were extracted avoiding the cracks (preventing contamination) and material from inner layers. μFTIR analysis, **Fig. 2c** shows characteristic absorption bands of substances related to environmental deposition and alteration (silicates, calcium carbonates, gypsum and calcium oxalates) but also to a protein-based substance (with absorption bands at 3300 cm^{-1} N-H stretching, $\sim 1650\text{ cm}^{-1}$ C=O stretching of amide I, $\sim 1540\text{ cm}^{-1}$ $-\text{NH}_2$ of amide II and $\sim 1450\text{ cm}^{-1}$ C-H deformation [4]). Selecting the areas containing a higher amount of protein, **Fig. 2c**, it is possible to relate it to an animal glue. In order to confirm this, a full chromatographic analysis would be needed.

The elimination of surface dirtiness is a first step during the restoration of art-works. However, this example has demonstrated that it is fundamental to identify the materials to the latest extend, as often distinguishing between the original coatings, dirt or the materials related to earlier restorations is not an easy task.

3.3 Beeswax from conservation treatments and wax from natural impurities of shellac

Wax is another kind of material that is often found in art-works. However, beeswax has also been employed in conservation treatments to consolidate paint layers. Beeswax is naturally secreted by the intra-abdominal glands of bees (*Apis mellifera* L.). The composition of beeswax is a complex mixture including saturated hydrocarbons, esters and 12-14% free fatty acids [25,26]. The presence of these fatty acids is responsible for the presence of reaction compounds such as carboxylates produced when the waxes come into contact with compounds containing metals. Wax may also be found in other materials produced by insect secretions such as the *Laccifer Lacca* Kerr. This resinous secretion, called Seed Lac once semi-refined, contains resin, dyes and 6-7% wax. Seed Lac is processed separating the wax, shellac wax, from the principally resinous part, shellac [27,28]. However, small wax impurities can still be found in shellac, principally used in varnishes and coatings.

From an historical restoration, a superficial treatment with beeswax is found on the canvas painting entitled *View of the Barcelona Port*, by Francesc Soler i Roviroa painted in 1890 (**Fig. 3**). It caused a tarnishing of the paint surface. After its identification has recently been partly eliminated. Various samples of this coating were

analysed by μ FTIR spectroscopy, obtaining different spectra showing that the layer is not homogeneous. After a meticulous separation the spectrum of the non-purified beeswax used was obtained. This kind of wax can be differentiated from the other natural waxes traditionally employed in artworks (purified beeswax and shellac wax) comparing it to the corresponding reference spectra (**Fig. 3a**) [29]. It has also been observed that it penetrated into the painting layers.

The waxes (**Fig. 3a**, Spectrum A) can be recognized by the ν C-H stretching vibrations of CH_2 bonds giving strong and narrow bands at 2918 and 2850 cm^{-1} and a small band at 2956 cm^{-1} due to the CH_3 group; sharp doublets at 1473 and 1463 cm^{-1} , indicating CH_2 bending vibrations; rocking vibrations at 729 and 719 cm^{-1} of methylene groups characteristic of a compound with a long aliphatic chain; and δ C-H bending vibrations in the 1475 - 1377 cm^{-1} region of an aliphatic compound. Non-purified beeswax presents a $\nu\text{C=O}$ stretching band at 1737 cm^{-1} and $\nu\text{C-O}$ stretching band at 1176 cm^{-1} of the ester and the band at 1712 cm^{-1} carboxylic groups (not present in purified beeswax) and in addition, a progression of absorption bands from 1300 to 1200 cm^{-1} , which are assigned to wagging and twisting vibrations of successive methylene groups coupled to a carboxyl group (not present in shellac wax) [29,30].

The presence of beeswax on the painting was therefore confirmed although the 1712 cm^{-1} band was unexpectedly small, a shoulder in the A spectrum of **Fig. 3a**. This is due, in part, the reaction of the beeswax fatty acids with the metals from the pigment particles, producing carboxylates. Zinc carboxylates are determined (bands at 1540 cm^{-1} , 1398 cm^{-1} and 1463 cm^{-1}) together with copper carboxylates in smaller amounts (1586 cm^{-1} band) [31,32] as is shown in **Fig. 3b**. The zinc is obtained from the lithopone (BaSO_4/ZnS), a filler from the chromatic layer. Additionally, the copper ions belong to the green pigment, copper acetoarsenite ($3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$), a synthetic pigment used in the 19th century and early 20th century [33]. Calcium carbonate is also determined from a chalk layer mixed with different colour pigments depending on the area directly applied over the canvas. This layer is porous in nature and thus, easily incorporates substances from the relatively thin (about $30\text{ }\mu\text{m}$) more superficial layers. The mixture of substances increases the complexity of the interpretation of the spectrum, and thus the best possible separation of materials is imperative to identify the several substances.

Fig.4a,b corresponds to the coating applied over a silver foil on a wood moulding from the 15th century altarpiece of Our Lady with the double intention of protecting and simulate gold [34]. The analysis of the coating identifies shellac containing shellac wax impurities. The two spectra are shown in **Fig. 4c**. A noteworthy difference between the two spectra is the shape and frequency position of the bands belonging to CH_3 and CH_2 stretching vibration at 2800 - 3000 cm^{-1} . In the shellac wax these bands are narrower due to the presence of numerous CH_2 groups showing long aliphatic chains from the wax compounds, and the corresponding frequencies are slightly lower owing to this. Some shellac bands hide the shellac wax bands. The residue of shellac wax in this artwork coating demonstrates that the shellac employed was of low purity.

3.4 Mixture of resin Pinaceae, drying oils and green copper pigment

A separation of resins and pigments is a challenge when analysing thin layers from small samples taken from coatings in art-works. It is more difficult when the resin is mixed with drying oils following ancient recipes of varnishes and coatings. The presence of various materials is responsible for their reaction and the production of new substances which often present similar absorption bands. Detecting the presence of oil or studying how the different materials age is possible using the sample preparation and the analytical methodology proposed. The results have been corroborated and extended using synchrotron radiation.

In order to illustrate this, a number of cases of study are shown. The first case corresponds to a sample extracted from a panel from the coffered ceiling of Paretdegada Chapel (La Selva del Camp, Catalonia) constituted by several painted wooden pieces of approximately 10x30 square cm. The panel is painted in blue and red with a white preparation layer and finished with a varnish coating (**Fig.5a**). Analysis of the varnish shows the presence of a *Pinus* resin, a common component of varnish (Spectrum A, **Fig. 5b**) [35]. Additionally, small variations in the spectrum are attributed to the presence of calcium oxalates (1640, 1320, 790 cm^{-1}) resulting from the alteration and/or environmental deposition (Spectrum B, **Fig.5b**) [36]

The *Pinus* specie used to obtain the colophony (diterpenic resin) is irrelevant since the differences between *Pinus* resins are determined only in fresh samples: the components are almost the same and there are only small differences in the relative proportions. During the aging process the differences between *Pinus* resins became gradually indiscernible since most of diterpene components are interconvertible to abietic acid, the most stable form. During the aging process, the abietic acid disproportionates forming dehydro- and dihydroabietic acid [13,37,38]. Therefore, aged colophony has a similar composition whatever its origin [39].

As a reference of aged colophony we took a lump of a residual secretion resin that was preserved in a knot of the wood identified as *Pinus* genus. The coffered ceiling is dated to the 14th century, thus giving a dating to the wood and the resin. The Infrared spectrum from this reference resin is shown in Spectrum I of **Fig.5b**. From this infrared spectrum the intensity of the absorption band at 1606 cm^{-1} should be noted. This band can be assigned to the stretching C=C and related to the aging process [30,40]. This band becomes more intense the more aged the resin. This is evidenced in Spectrum II of **Fig. 5b** that corresponds to a 100 year old *Pinus* resin obtained from the Kew gardens collection. Moreover, it is also observed, that the 2950 cm^{-1} band corresponding to the $\nu\text{C-H}$ stretching bands of methyl and methylene groups (2800-3000 cm^{-1} bands), gained intensity, when the *Pinus* resin was very old. A useful process of curve fitting can separate overlapped bands into a reasonable number of component bands (**Fig. 6a,b**). Additionally, the 1699 cm^{-1} band widens and the maximum moves to higher wave numbers with a new maximum of 1716 cm^{-1} due to the presence of the $\text{R}_2\text{C=O}$ group related to the colophony oxidised compounds 7-oxo dehydroabietic, 7,15-dihydroxy dehydroabietic and 15-hydroxy-7-dehydroabietic [41]. Taking this into account, the infrared spectrum corresponding to the varnish of the coffered ceiling corresponds to a newer resin, as the 1606 cm^{-1} band, is less intense and the split of the bands previously cited is not very important, indicating that the varnish is not the original but was most probably applied at a later date.

As a final case, the characterizations of the coatings which are dark/black amber in colour from motifs of the polychrome decoration from the wood on the desks were found to be a copper resinate (**Fig.7a**).

Besides the aging process, with copper resins it is necessary to consider also the reactivity among the several components and also with the environment (agents and pollutants). Copper resins are produced by mixing a resin from the *Pinus* with a green copper pigment, such as the copper II acetate monohydrate [42]. This copper pigment shows the tendency to produce copper carboxylates from the reaction with the abietic acid and abietane skeleton acids, [43-45]. This can be observed in the analysis of the sample extracted from the decorations of a desk from the 17th century (Museu del Disseny de Barcelona). The copper resinate is applied over a silver metal foil to highlight certain motifs of the decoration. Moreover, in order to assure the stability of these metal foils against corrosion and give it a metallic like glossy finish, these coatings were applied over the metallic foil. The thickness of the resin layer is 50 micrometers.

The resin layer looks like a dark material, with a brown shade. When observed under the optical microscope, it appears heterogeneous and in the green coloured area discrete green particles can be distinguished, **Fig. 7b**. **Figure 7c** shows an infrared spectrum recorded from a single green particle showing that it corresponds to a copper II acetate monohydrate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (called verdigris). The matrix identified as a *Pinus* resin shows a green shade and in some areas is more amber in colour with a similar appearance to the varnish of the last case shown. The intensity of the 1610 cm^{-1} (1612 cm^{-1}) band, more discernible in the green areas (Spectrum B in **Fig.7c**), is characteristic of antisymmetric stretching of COO^- group of copper carboxylates from abietic acid and abietane skeleton acids [30]. Thus, in the 1600 cm^{-1} region, absorption bands of these copper carboxylates and $\text{C}=\text{C}$ stretching band related to the aging of the *Pinus* resin are overlapped. In this case the $\sim 2950\text{ cm}^{-1}$ is not very important and indicates that the aging of the resin is only scarcely perceptible. However, with respect to the aged *Pinus* resin, a new band at 1400 cm^{-1} which can also be associated with symmetric stretching of COO^- group of copper abietate appears (Spectrum B in **Fig.7c**) [30]. The distribution map of these compounds can be observed in **Figure 8a**. The sample was prepared by cutting a thin layer of resin, with the use of precision cutting instruments –microknife, of an area that includes pigment particles visible under optical microscopy. The thin layer fragment was squeezed between two diamond windows, spreading the sample; with this method it is possible to maintain the location of the compounds.

A similar case but showing some differences is observed from a sample from an early 20th century desk. In the spectra obtained by μFTIR two maxims are observed, one at about 2870 cm^{-1} and another at 2856 cm^{-1} . On the basis of spectral features this is indicative of the presence of other substances. This is shown in $\mu\text{SR-FTIR}$ spectra after adequate curve fitting processing (Spectrum C in **Fig.7c,e** and **Fig. 6d**). Moreover, the weak band at 1585 cm^{-1} observed in μFTIR spectrum is related to the antisymmetric stretching of COO^- group from copper fatty carboxylate acids [5,36]. From the analysis carried out with $\mu\text{SR-FTIR}$, it can be concluded that copper carboxylates are formed from the saturated fatty acids of the drying oil. In Spectrum D in **Fig. 7c-e** strong and narrow bands at 2918 and 2850 cm^{-1} of C-H stretching vibrations of CH_2 bonds, a small band at 2956 cm^{-1} of C-H stretching vibrations of CH_3 , a CH_2 bending vibration band at

$\sim 1470\text{ cm}^{-1}$ and a weak CH_2 rocking band at 721 cm^{-1} and the strong band at 1585 cm^{-1} are observed. It is important to note that, in this case fewer pigment relics remain (copper II acetate monohydrate) and in the area around the pigment particles, copper carboxylates formed by the reaction with the fatty acids are found (**Fig.8b**). This demonstrates how for carboxylates to be produced, it is necessary that the oil has already begun aging and thus producing free fatty acids. When this happens, the matrix is not very fluid and this carboxylates cannot readily diffuse. Thus in this area copper carboxylates formed from the fatty acids and from the abietic acid and abietane skeleton acids coexist. Noteworthy is the areas where copper carboxylates formed from the fatty acids are determined copper oxalates are also found in small quantities. Determination of reaction compounds allow to deduce what the original substances were which now are not present or cannot be detectable.

All these results are in good agreement with the category of analysed objects. The *Pinus* resin was a cheap material used to varnish daily objects like furniture, household items, large surfaces... thus, it is reasonable to find it coating such ordinary objects like a desk or a coffered ceiling [24]. The fact that in some cases only the resin has been found can be explained by the fact that the varnish, made of resin, was dissolved in essential oil. During drying and aging the volatile compounds from the essential oil disappear and cannot be detected by μFTIR . This kind of varnish was used from the 15th century, and often mentioned in historical documents [2]. Oleo-resin varnish, which is a very common varnish, used since the 9th century (at least) and has been cited in art treatises and manuscripts throughout the ages [2,46].

4. Conclusions

The varnishes, protections and coloured coatings of art-works are thin surface layers made up of complex materials of different nature. These surface layers often contain the original substances, reaction and aging products, environmental deposits or compounds applied in later restorations. To succeed in the analysis of these layers, the complex composition and the micro-layer structure must be taken into consideration. Micro infrared spectroscopy in transmission mode is proposed as the first step for the study of such layers, although the results obtained are often definitive such as in the case where guanine was determined. The importance of sample extraction after the object has been meticulously observed is highlighted in the second case shown where a protein-based coating to give to the nuances the brilliance of gold is determined. Additionally, it verified the information found in ancient treatises with regard to gilding techniques. The other cases shown demonstrate the range of problems that can be solved by μFTIR spectroscopy; i.e. discriminating substances in complex matrixes from very small samples and even with substances that are chemically similar. For instance the beeswax reaction compounds have been determined. For the discrimination of the different types of substances forming heterogeneous samples, a meticulous examination of the line shape of the spectra and band separation of highly overlapped bands are necessary. The importance of having aged reference material as similar as possible to the real samples is underlined. Furthermore, having materials differently aged is an aid in the interpretation of the spectra obtained. Some mathematical tools such as, distribution maps of specific infrared bands and curve fitting, favour the interpretation of the spectra and help to elucidate the various substances present in a complex sample. The improved

characteristics of μ FTIR with synchrotron radiation improve the spatial resolution obtained which is particularly important in the analysis of heterogeneous samples. Moreover, it produce the high quality spectra necessary for the identification of small spectral features while comparing to the data obtained with conventional techniques and thus, provides more reliability. Finally, through the identification of individual bands it has been possible to comprehend the interaction processes occurring during the aging of *Pinus* resin, dying oil and green copper pigment mixtures.

References

- [1] E.R. de la Rie, Old Master paintings: a study of the varnish problem, *Anal. Chem.* 61 (1989) 1228A-1240A.
- [2] C.L. Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, Ed Dover Publications Inc., Mineola, New York 2001.
- [3] F. Caruso, S. Orecchio, M.G. Cicero, C. Di Stefano, Gas chromatography mass spectrometry characterization of the varnish and glue of an ancient 18th century double bass, *J. Chromatogr. A* 1147 (2007) 206-212.
- [4] M.R. Derrick, S. Stulik, J.M. Landry, *Scientific Tools for Conservation Infrared Spectroscopy in Conservation Science*, J. Paul Getty Trust, Los Angeles, 1999.
- [5] N. Salvadó, S. Butí, M.J. Tobin, E. Pantos, A.J.N.W. Prag, T. Pradell, Advantages of the Use of SR-FT-IR Microspectroscopy: Applications to Cultural Heritage, *Anal. Chem.* 77 (2005) 3444-3451.
- [6] J. Font, N. Salvadó, S. Butí, J. Enrich, Fourier transform infrared spectroscopy as a suitable technique in the study of the materials used in waterproofing of archaeological amphorae, *Anal. Chim. Acta.* 598 (2007) 119-127.
- [7] C. Daher, C. Paris, A.S. Le Ho, L. Bellot-Gurlet, J.P. Echard, A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes, *J. Raman Spectrosc.* 411 (2010) 494-1499.
- [8] H. Schulz, M. Baranska, Identification and quantification of valuable plant substances by IR and Raman spectroscopy, *Vib. Spectrosc.* 43 (2007) 13-25.
- [9] M. Derrick, Fourier Transform Infrared Spectral Analysis of Natural Resins Used in Furniture Finishes, *Journal of the American Institute for Conservation*, 28 (1989) 43-56.
- [10] *Organic Mass Spectrometry in Art and Archaeology*. M.P. Colombini, F. Modugno (Eds.) John Wiley & Sons, Pisa, 2009.
- [11] M.T. Doménech-Carbó, Novel analytical methods for characterising binding media and protective coatings in artworks, *Anal. Chim. Acta.* 621 (2008) 109-139.
- [12] M. Cotte, P. Dumas, Y. Taniguchi, E. Checroun, P. Walter, J. Susini, Recent applications and current trends in Cultural Heritage Science using synchrotron-based Fourier transform infrared microspectroscopy, *C. R. Physique* 10 (2009) 590-600.
- [13] J.S. Mills, R. White, *The organic chemistry of museum objects*, 2ⁿ ed., Butterworths, Oxford, 1994.
- [14] L.L. Steele, Abietic acid and certain metal abietates, *J. Am. Chem. Soc.* 44 (1922) 1333-1341.
- [15] <http://www.museudeldisseny.cat> (accessed 26 May 2014)
- [16] <http://www.mmb.cat/> (accessed 26 May 2014)
- [17] G. Cinque, M. Frogley, K. Wehbe, J. Filik, J. Pijanka, Multimode InfraRed Imaging and Microspectroscopy (MIRIAM) Beamline, *Diamond Synchrotron Radiation News* 24 (2011) 24-33. DOI10.1080/08940886.2011.618093
- [18] P.R. Griffiths, J.A. de Haseth, *Fourier Transform Infrared Spectrometry*, 2nd ed., Wiley-Interscience, Hoboken, New Jersey, 2007.
- [19] R. Pedro Lopes, M. Paula, M. Marques, R. Valero, J. Tomkinson, L.A.E. Batista de Carvalho, Guanine: A combined study using vibrational spectroscopy and theoretical methods, *Spectrosc-int J*, 27 (2012) 273-292.
- [20] A.R. Mirhabibi, *Ceramic coatings for pigments, ceramic coatings applications in engineering*, Feng Shi (Ed.) ISBN: 978-953-51-0083-6, In Tech., 2012.
- [21] F.J. Maile, G. Pfaff, P. Reynders, Effect pigments- past, present and future, *Prog. Org. Coat.* 54 (2005) 150-163.

- [22] G. Pfaff, P. Reynders, Angle-dependent optical effects deriving from submicron structures of films and pigments, *Chem. Rev.* 99 (1999) 1963-1981.
- [23] I.C.A. Sandu, M.H. de Sá, M. Costa Pereira, Ancient “gilded” art-objects from European cultural heritage: A review on different scales of characterization, *Surf. Interface. Anal.* 43 (2011) 1134-1151.
- [24] M.P. Merrifield, *Medieval and Renaissance Treatises on the arts of painting: Original Texts with English Translations*, Dover publications, Inc., Mineola, New York, 1999.
- [25] R. Buchwald, M.D. Breed, L. Bjostad, B.E. Hibbard, A.R. Greenberg, The role of fatty acids in the mechanical properties of beeswax, *Apidologie* 40 (2009) 585-594.
- [26] A. Tulloch, Beeswax: structure of the esters and their component hydroxyl acids and diols, *Chemistry and physics of lipids, Chem. Phys. Lipids* 1 (1971) 235-265.
- [27] M.S. Wadia, R.G. Khurana, V.V. Mhaskar, S. Dev Chemistry of Lac Resin-I, *Tetrahedron*, 25 (1969) 3841-3853.
- [28] E. Faurot-Bouchet, G. Michel, Composition of Insect Waxes. I. Waxes of Exotic Coccidae: *Gascardia Madagascariensis*, *Coccus Ceriferus* and *Tachardia Lacca*, *The Journal of the American Oil Chemists Society*, 41(1964) 418-421.
- [29] M. Regert, S. Colinart, L. Degrand, O. Decavallas, Chemical alteration and use of beeswax through time: accelerated ageing tests and analysis of archaeological samples from various environmental contexts, *Archaeometry* 43 (2001) 549-569.
- [30] *The infrared spectra of complex molecules*, vol. 1, 3rd ed., L. J. Bellamy, Halsted Press, a division of John Wiley & Sons, Inc., New York, 1975.
- [31] R. Mazzeo, S. Prati, M. Quaranta, E. Joseph, E. Kendix, M. Galeotti, Attenuated total reflection micro FTIR characterisation of pigment-binder interaction in reconstructed paint films, *Anal. Bioanal. Chem.* 392 (2008) 65-76.
- [32] S. Barmen, S. Vasudevan, Melting of Saturated Fatty acid zinc soaps, *J. Phys. Chem. B*, 110 (2006) 22407-22414.
- [33] I. Fielder, M.A. Bayard, Esmerald green and Scheele’s Green, in: E. West FitzHugh (Ed.), *Artist’ Pigments*, vol. 3, National Gallery of Art, Washington and Archetype Publications, London, 1983, pp. 219-271.
- [34] N. Salvadó, S. Butí, A. Labrador, G. Cinque, H. Emerich, T. Pradell, SR-XRD and SR-FTIR study of the alteration of silver foils in medieval paintings, *Anal. Bioanal. Chem.* 399 (2011) 3041-3052.
- [35] J.S. Mills, R. White, *Natural Resins of Art and Archaeology: their Sources, Chemistry, and Identification*, *Stud. Conserv.* 22 1977 12-31.
- [36] N. Salvadó, S. Butí, J. Nicholson, H. Emerich, A. Labrador, T. Pradell, Identification of reaction compounds in micrometric layers from gothic paintings using combined SR-XRD and SR-FTIR, *Talanta* 79 (2009) 419-428.
- [37] A. Enoki, Isomerisation and autooxidation of resin acids, *Wood Res.* 59, 60 (1976) 49–57.
- [38] G. Steigenberger, C. Herm, Natural resins and balsams from an eighteenth-century pharmaceutical collection analyzed by gas chromatography/mass spectrometry, *Anal. Bioanal. Chem.* 401 (2011) 1771-1784.
- [39] D. Scalarone, M. Lazzari, O. Chiantore, Ageing behaviour and pyrolytic characterisation of diterpenic resins used as art materials: colophony and Venice turpentine, *J. Anal. Appl. Pyrol.* 64 (2002) 345–361.
- [40] E. Pretsch, P. Bühlmann, C. Affolter, A. Herrera, R. Martínez, *Determinación estructural de compuestos orgánicos*, Elsevier Masson D.L., Barcelona, 2009.
- [41] K.J. van den Berg, J.J. Boon, I. Pastorovay, L.F.M. Spetter, Mass spectrometric methodology for the analysis of highly oxidized diterpenoid acids in Old Master paintings, *Journal of Mass Spectrometry*, *J. Mass. Spectrom.* 35 (2000) 512-533.
- [42] N. Salvadó, S. Butí, M. Cotte, G. Cinque, T. Pradell, Shades of green in 15th century paintings: combined microanalysis of the materials using synchrotron radiation XRD, FTIR and XRF, *Appl. Phys. A*, 111 (2013) 47-57.
- [43] M. Gunn, G. Chottard, E. Rivière, J.J. Girerd, J.C. Chottard, Chemical reactions between copper pigments and oleoresinous media, *Stud. Conserv.* 47 (2002) 12-23.
- [44] R. Woudhuysen-Keller, Aspects of painting technique in the use of verdigris and copper resinate, in: Wallert A, Hermans E, Peek M. (Eds.), *Historical Painting Techniques, Materials and Studio Practice*, Getty Conservation Institute, 1995 65-69.
- [45] H. Kühn, Verdigris and copper resinate, in: A. Roy (Ed.), *Artists’ Pigments: A Handbook of Their History and Characteristics*, vol. 2, Oxford University Press, New York, 1993, pp. 131-147.
- [46] *Mappae clavicula: a little key to the world of medieval techniques*, the American Philosophical Society, Philadelphia, 1974.

Acknowledgements

N. Salvadó and S. Butí received financial support under MICINN (Spain), grant HAR2009-10790 and under Generalitat de Catalunya, grant 2009SGR01251. We thank Diamond Light Source for access to beamline MIRIAM B22 (SM8992 and SM8153) that contributed to the results presented here. The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 226716.

Part of this work was carried out within the framework of agreements of collaboration between the Universitat Politècnica de Catalunya (UPC) and the "Centre de Restauració de Béns Mobles de Catalunya" (CRBMC). The authors thank the "Escola d'Art i Disseny de la Diputació de Tarragona" in Tortosa, the "Museu del Disseny de Barcelona" and "Museu Marítim de Barcelona" in Barcelona and "Vinseum" in Vilafranca del Penedès, for having allowed us access to the art works.

We would also like to thank the "Economic Botany Collection of the Royal Botanic Gardens, Kew", in London, for supplying aged material and Master Violin Maker, José María Lozano, for supplying resin materials.

Figure captions

Figure 1.

Sample taken from the inner coating material of a 16th century hope chest: a) optical microscope image of sample; b) μ FTIR spectra from sample (measured area 50x50 μ m), guanine identified in Spectrum A and protein identified in Spectrum B; c) 700-2000 cm^{-1} region of spectrum A.

Figure 2.

Sample taken from gilding area of a 17th century altarpiece from Tortosa Cathedral: a) Dark field OM image from the surface of the sample. b) Backscattered SEM image from a sample fragment put in perspective; this image shows the face surface that consists of a layer of thickness less than 2 μ m. c) μ FTIR spectra from superficial layer (measured area 50x50 μ m); a mixture of protein, silicates, gypsum, calcium carbonate and calcium oxalates are identified in *Spectrum I* and only characteristic protein absorption bands are shown in *Spectrum II*.

Figure 3.

Sample taken from superficial material of 19th century canvas painting "View of the Barcelona Port" by Francesc Soler i Rovirosa: a) μ FTIR spectra (measured area 50x50 μ m) of shellac wax (*Spectrum I*), microcrystalline wax (*Spectrum II*), beeswax (*Spectrum III*) from reference materials and beeswax spectrum identified in the superficial layer (*Spectrum A*). b) 1300-1650 cm^{-1} region of sequence of spectra related to the compounds identified in the superficial layer is shown. c) Detail of the canvas painting before restoration process (before removing beeswax treatment).

Figure 4.

Sample taken from simulated gilding area of a 15th century altarpiece. a) Dark field OM image from a polished cross-section of the sample. Sequence of layers from bottom to top: gypsum ground layer, bole layer, silver foil, coating layer. b) Ultraviolet light OM image from a polished cross-section of the sample. c) μ SR-FTIR spectra from coating layer (measured area 12x12 μ m); shellac resin (*Spectrum A*) and mixture of shellac resin and shellac wax (*Spectrum B*).

Figure 5

Sample taken from varnish layer of 14th century coffered ceiling from Paredelgada Chapel: a) Stereomicroscope image of sample, sequence of paint layers is shown. b) μ FTIR spectra of *Pinus* resin from knot in the wood (*Spectrum I*), 100 years old *Pinus sylvestris* resin (*Spectrum II*), varnish spectrum corresponding to *Pinus* resin (*Spectrum A*), varnish spectrum corresponding to *Pinus* resin and calcium

oxalates (*Spectrum B*). Spectra I and II have been used as references. (Spectra I,II and A, B measured area 100x100 μm and 50x50 μm , respectively)

Figure 6

Curve fitting of C-H stretching bands of methyl and methylene groups a) of *Pinus* resin from knot in the wood of 14th century (part of *Spectrum I* in Fig. 5b), b) 100 years old *Pinus sylvestris* resin (part of *Spectrum I* in Fig. 5b), c) varnish of *Pinus* resin (part of *Spectrum A* in Fig. 5b) and d) oil-resin coating, mixture of *Pinus* resin and drying oil (part of *Spectrum C* in Fig. 7).

Figure 7

Samples taken from coating layers of 17th and 20th century desks: a) Scheme of sequence of layers. b) Stereomicroscope image of green coating sample of 17th century desk; obverse and reversed with remains of silver foil. c) μFTIR spectra (measured area 100x100 μm) of 100 years old *Pinus sylvestris* resin (*Spectrum II*) and copper abietate (*Spectrum III*); $\mu\text{SR-FTIR}$ spectra (measured area 12x12 μm) of green pigment particle of sample of 17th century desk corresponding to $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (*Spectrum A*), of green coating sample of 17th century desk corresponding to *Pinus* resin and copper carboxylates of abietic acid and abietanes skeleton acids (*Spectrum B*), of green coating sample of 20th century desk corresponding to *Pinus* resin and drying oil (*Spectrum C*), of green coating sample of 20th century desk corresponding to copper carboxylates from fatty acids and from abietic acid and abietane skeleton acids (*Spectrum D*). d) 1300-1800 cm^{-1} region of COO- stretching bands. e) 2500-3200 cm^{-1} region of spectra of C-H stretching bands of methyl and methylene groups.

Figure 8.

Optical image of a sample fragment spread on diamond window and substance distribution IR map obtained in transmission mode. Spot size: 12x12 μm . IR intensity maps, higher: white –lower: blue. a) Green copper pigment $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ –intensity map of 690 cm^{-1} band-, *Pinus* resin –intensity map of 1700 cm^{-1} band- and copper abietate–intensity map of 1400 cm^{-1} band- of sample taken from coating layer of 17th century desk. Map I size: 45x71 μm^2 , 10x12 measurements and map II size: 48x96 μm^2 , 10x15 measurements. b) Green copper pigment $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ –intensity map of 3375 cm^{-1} band-, *Pinus* resin –intensity map of 2870 cm^{-1} band-and copper carboxylates from fatty acids–intensity map of 1585 cm^{-1} band- of sample taken from coating layer of 20th century desk. Map size: 60x46 μm^2 , 8x6 measurements.

Figure 1.

Sample taken from the inner coating material of a 16th century hope chest: a) optical microscope image of sample; b) μ FTIR spectra from sample (measured area 50x50 μm), guanine identified in Spectrum A and protein identified in Spectrum B; c) 700-2000 cm^{-1} region of spectrum A.

Figure 2.

Sample taken from gilding area of a 17th century altarpiece from Tortosa Cathedral: a) Dark field OM image from the surface of the sample. b) Backscattered SEM image from a sample fragment put in perspective; this image shows the face surface that consists of a layer of thickness less than 2 μm . c) μFTIR spectra from superficial layer (measured area 50x50 μm); a mixture of protein, silicates, gypsum, calcium carbonate and calcium oxalates are identified in *Spectrum I* and only characteristic protein absorption bands are shown in *Spectrum II*.

Figure 3.

Sample taken from superficial material of 19th century canvas painting “View of the Barcelona Port” by Francesc Soler i Rovirosa: a) μ FTIR spectra (measured area 50x50 μm) of shellac wax (*Spectrum I*), microcrystalline wax (*Spectrum II*), beeswax (*Spectrum III*) from reference materials and beeswax spectrum identified in the superficial layer (*Spectrum A*). b) 1300-1650 cm^{-1} region of sequence of spectra related to the compounds identified in the superficial layer is shown. c) Detail of the canvas painting before restoration process (before removing beeswax treatment).

Figure 4.

Sample taken from simulated gilding area of a 15th century altarpiece. a) Dark field OM image from a polished cross-section of the sample. Sequence of layers from bottom to top: gypsum ground layer, bole layer, silver foil, coating layer. b) Ultraviolet light OM image from a polished cross-section of the sample. c) μSR-FTIR spectra from coating layer (measured area 12x12 μm); shellac resin (*Spectrum A*) and mixture of shellac resin and shellac wax (*Spectrum B*).

Figure 5

Sample taken from varnish layer of 14th century coffered ceiling from Paretdegada Chapel: a) Stereomicroscope image of sample, sequence of paint layers is shown. b) μ FTIR spectra of *Pinus* resin from knot in the wood (*Spectrum I*), 100 years old *Pinus sylvestris* resin (*Spectrum II*), varnish spectrum corresponding to *Pinus* resin (*Spectrum A*), varnish spectrum corresponding to *Pinus* resin and calcium oxalates (*Spectrum B*). Spectra I and II have been used as references. (Spectra I,II and A, B measured area 100x100 μ m and 50x50 μ m, respectively)

Figure 6

Curve fitting of C-H stretching bands of methyl and methylene groups a) of *Pinus* resin from knot in the wood of 14th century (part of *Spectrum I* in Fig. 5b), b) 100 years old *Pinus sylvestris* resin (part of *Spectrum I* in Fig. 5b), c) varnish of *Pinus* resin (part of *Spectrum A* in Fig. 5b) and d) oil-resin coating, mixture of *Pinus* resin and drying oil (part of *Spectrum C* in Fig. 7).

Figure 7

Samples taken from coating layers of 17th and 20th century desks: a) Scheme of sequence of layers. b) Stereomicroscope image of green coating sample of 17th century desk; obverse and reversed with remains of silver foil. c) μFTIR spectra (measured area $100 \times 100 \mu\text{m}$) of 100 years old *Pinus sylvestris* resin (*Spectrum II*) and copper abietate (*Spectrum III*); $\mu\text{SR-FTIR}$ spectra (measured area $12 \times 12 \mu\text{m}$) of green pigment particle of sample of 17th century desk corresponding to $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (*Spectrum A*), of

green coating sample of 17th century desk corresponding to *Pinus* resin and copper carboxylates of abietic acid and abietanes skeleton acids (*Spectrum B*), of green coating sample of 20th century desk corresponding to *Pinus* resin and drying oil (*Spectrum C*), of green coating sample of 20th century desk corresponding to copper carboxylates from fatty acids and from abietic acid and abietane skeleton acids (*Spectrum D*). d) 1300-1800 cm⁻¹ region of COO⁻ stretching bands. e) 2500-3200 cm⁻¹ region of spectra of C-H stretching bands of methyl and methylene groups.

Figure 8.

Optical image of a sample fragment spread on diamond window and substance distribution IR map obtained in transmission mode. Spot size: 12x12 μm . IR intensity maps, higher: white –lower: blue. a) Green copper pigment $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ –intensity map of 690 cm^{-1} band-, *Pinus* resin –intensity map of 1700 cm^{-1} band- and copper abietate–intensity map of 1400 cm^{-1} band- of sample taken from coating layer of 17th century desk. Map I size: 45x71 μm^2 , 10x12 measurements and map II size: 48x96 μm^2 , 10x15 measurements. b) Green copper pigment $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ –intensity map of 3375 cm^{-1} band-, *Pinus* resin –intensity map of 2870 cm^{-1} band-and copper carboxylates from fatty acids–intensity map of 1585 cm^{-1} band- of sample taken from coating layer of 20th century desk. Map size: 60x46 μm^2 , 8x6 measurements.

Highlights

- micro-FTIR approach for the study of micro samples of coatings from the art-works
- strategy for identification of organic, inorganic, reaction and aging compounds
- identification of guanine (nucleic acid base) unexpected pigment in art-works
- distribution IR maps can shed light on how reaction compounds have been distributed
- interaction processes study during the aging of *Pinus* resin-oil-pigment mixtures