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REVIEW

COMBINATION OF FTIR AND X-RAYS SYNCHROTRON-BASED MICRO-IMAGING TECHNIQUES FOR THE STUDY OF ANCIENT PAINTINGS. A PRACTICAL POINT OF VIEW

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Applications of FTIR to the study of ancient paintings have encountered two major steps: the development of FTIR microscopes, which enable to watch the sample and to select the regions of interest; and the migration of those FTIR microscopes towards synchrotron facilities, that offers a significant improvement in terms of spatial resolution and spectral quality. Even if access to synchrotrons is by nature limited, it is worth applying for such installations as they usually provide a set of micro-imaging techniques. FTIR end-stations should then be considered as part of a wider analytical platform. Combining micro FTIR with micro X-ray fluorescence, micro X-ray diffraction or micro X-ray absorption spectroscopy for the study of paintings enables a deeper insight into paintings at the micrometer scale. Several examples of X-ray/infrared combinations are given. The focus is given to practical aspects, in particular to the critical issue of sample preparation. Alternatives to the classical polished cross-sections are proposed and evaluated. Data treatment is also discussed.

1   Introduction

1.1   Vibrational techniques for the analysis of paintings

Vibrational techniques such as FTIR and Raman are now well established in the field of Cultural Heritage, as illustrated by the increasing number of participants to the IRUG conferences.[1] These methods are particularly relevant for the analysis of ancient paintings as they offer an hybrid probe, exciting both organic and inorganic compounds hence providing the possibility to identify in a single analysis both pigments, binders, varnishes, mortars…

The development of infrared and Raman microscopes was a real asset as it offered the possibility to visualize the sample, and to spot the area (single point, profile or 2D map) to be analysed. Chemical mapping is thus generated and can complement morphological observations made with photonic or electron microscopes.

While Raman offers micrometric lateral resolution, infrared microscopy is often limited by source brightness. Synchrotron sources enable us to overcome this aspect as they provide bright and collimated infrared beams. With such installations, the spot size can be reduced down to the diffraction limit (half wavelength), without significant loss of flux. This advantage explains the growing number of synchrotron infrared end stations worldwide (around 25 end-stations in March 2008).

1.2 Synchrotron-based micro-imaging techniques for the analysis of paintings

Synchrotron storage rings are primarily bright X-ray sources. In this context, infrared emission can be perceived as merely a kind of useful "by-product". X-ray and infrared micro-imaging techniques benefit from the same characteristics of synchrotron sources: mainly bright and polychromatic. The brightness is essential to obtain high-resolution 2D mappings which require a simultaneous small probe, small dwell time and high signal-to-noise ratio. The continuous and extended energy range is indispensable to perform spectroscopic analyses (FTIR and X-ray absorption spectroscopy). It is also an advantage for the optimization of micro X-ray fluorescence and micro X-ray diffraction experiments. X-ray and infrared imaging techniques are based on different spectroscopy modalities, consequently they offer complementary information. It can be very useful to combine these various methods and to consider the different microscopes as part of a whole multi-modal platform.

Hereafter we give several examples of X-ray/infrared combinations applied to the analysis of fragments of paintings as well as cultural objects such as African statues. The focus is on three X-ray techniques: micro X-Ray Fluorescence (µXRF), micro X-ray Absorption Near Edge Spectroscopy (µXANES) and micro X-Ray Diffraction (µXRD). **µXRF** provides elemental mapping with high sensitivity. It is a useful technique to track trace elements. It was recently used to image chlorine distribution in blackening cinnabar paintings from Pompeii[2] and from the Pedralbes monastery.[3] Combined with µXANES, chemical mappings can be generated by acquiring fluorescence mappings at escence mappings at pertinent excitation energies. **µXANES** is a key method to identify pigments[4] or alteration products[2-3] since it allows the selective analysis of a single element, even in diluted and amorphous state. It would certainly find a lot of applications for the elucidation of unknown pigments as well as for the better understanding of alteration phenomena, not only in paintings but also in many other cultural heritage applica-

tions (glass, paper, metal…). The interest of µXRD is to offer the identification of crystallized phases with high sensitivity. For the analysis of paintings, lateral resolution and data quality are the key points that enable the detection of pigments even in low concentration and with low reflecting power.[5]

1.3 Sample preparation: a key issue

Imaging techniques are particularly suited for the analysis of painting fragments since paintings often present a multi-layered arrangement (with mortar, rendering layer, size layer, ground layer, priming layer, coloured layers, varnishes, conservation layer, superficial pollution, degradation…). Polished cross-sections are a classic way to reveal the whole painting stratigraphy: a painting fragment is embedded in resin and the resin block is milled or polished, perpendicularly to the painting surface until reaching the entire set of layers. This process is very conventional for observation with photonic or electron microscope. It is also adapted for Raman which is based on a superficial analysis. Yet it is not necessarily adapted for analysis by micro-FTIR: the two main drawbacks being that it impedes working in transmission and that the organic embedding resin may diffuse inside the sample, hampering the identification of the original organic compounds. In this article, different modalities for sample preparation are reviewed in the particular context of combined synchrotron-based infrared and X-rays analyses.

2 Sample preparation: versatile vs. customized approaches

2.1 General considerations

The combination of different analytical techniques applied to the same object leads to a specific experimental challenge dealing with sample preparation: preparing several samples, adapted to the specifications of each technique; or preparing a single sample, globally compatible with the requirements of different techniques. An additional choice must be done: working on "thick" samples (polished samples, even entire objects), in "reflection" mode; or working on "thin" samples (fragments, thin sections) in "transmission" mode. A detailed scheme of set-ups optimised for each technique can be found elsewhere.[3]

µXRF and µ-Raman probes are surface-sensitive (with different penetration depths). Hence, for these techniques, polished sections are preferred, and caution must be paid to surface quality, which can have a high impact on data quality. µXRD and µFTIR can also be performed on polished section in "reflection" mode, yet, working in transmission significantly

improves data quality. Thin sections are usually better suited in the case of a µFTIR/µXRD combination. The technical requirements are different; details are given hereafter. For µXRD, the X-ray penetration can be sufficient to work in transmission across a polished fragment embedded in resin thus providing an alternative to the complex preparation of thin sections. For µXANES, working on thin sections can be relevant as long as the element of interest is sufficiently concentrated. Dwell time, and consecutively possible radiation damages can be significantly decreased by working in transmission on thin sections.

2.2 Preparation and analysis of polished sections

This preparation certainly offers the best stratigraphy quality, and is compatible for many analyses (visible and electron microscopy mainly). Most of painting analyses, performed by µXRF, are carried out on polished sections.[2,4] The main drawback for FTIR analysis is that working in the transmission mode is hindered. The two classic FTIR set-ups developed for measuring infrared absorption at the surface of a sample are ATR and reflection. For the moment and to our knowledge, the use of a synchrotron source for ATR measurements on paintings has not been reported yet. Indeed, ATR coupled to a focal array detector is competing with synchrotron radiation in terms of lateral resolution.[6] The combination of synchrotron sources with such equipment is ongoing. Recent developments of new ATR objectives will certainly lead to a real revolution for the study of polished cross-sections.

Performing FTIR in reflection mode has two main advantages: quite easy sample preparation and quite easy microscope alignment (comparing with the more tricky alignment of confocal microscope in transmission). The main drawback is related to data quality, FTIR spectra being quite noisy (depending on flux, aperture size and sample composition), and distorted. In some cases, spectra identification will be rather delicate, because databases usually provide spectra acquired in transmission. Yet, it can be useful under certain circumstances, in particular when the study aims more at visualizing the distribution of compounds than at their identification identifying. This approach was followed to image organic components in patina covering the surface of ritual African statues.[7-8] These patinas are made of mineral and organic conpounds and they can be so hard and brittle that pressing or cutting them is impossible. Transversal cross-sections were obtained with an ultra-microtome. The sectioned fragments were too fragile to stand alone after cutting. The interest of the ultra-microtome was to provide a very high quality surface
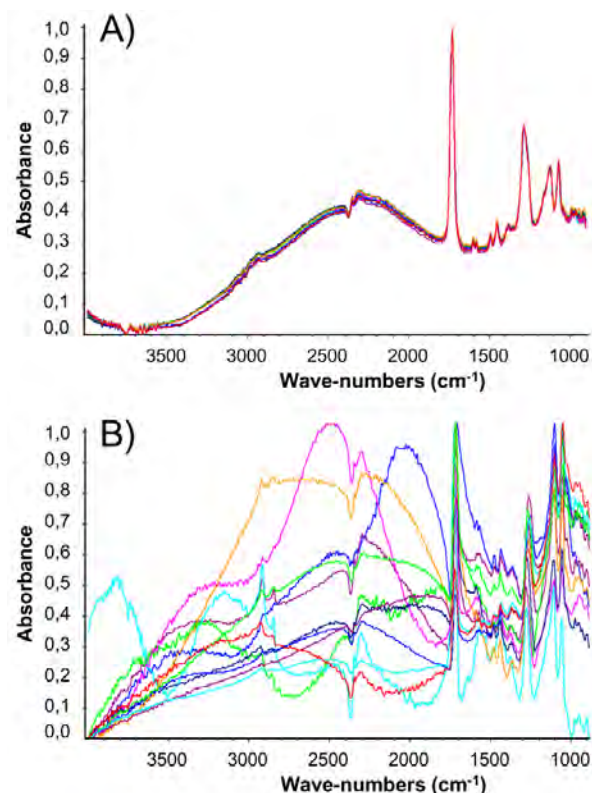

Figure 1: Reproducibility of FTIR spectra acquired in reflection on the surface of a resin block when the surface is obtained, A) by cutting with an ultra-microtome, B) by polishing with silicon carbide (grade 1200). Aperture size: 12×12 µm².

of the remaining block. Figure 1 demonstrates the dramatic effect of surface quality: ten FTIR spectra were collected in reflection, with a beam size of 12×12 µm², at the surface of a polyester resin block. In Fig. 1A, the surface of the resin block was obtained with an ultra-microtome. Spectra are very reproducible. In Fig. 1B, the surface was obtained by polishing with silicon carbide (grade 1200). The resulting surface is much more irregular, leading to more distortions and variations between FTIR spectra. This issue is even more critical with small beams, and can be tolerated while working with classical Globar sources and consequently larger probes.

In the example of African statues, an additional micro-analytical technique (ToF-SIMS) was used, making sample preparation even more critical. Besides, µXRF and µXANES were performed at the iron K-edge in order to distinguish between organic and mineral iron, and to evaluate the possible presence of traces of blood in these patinas. Such polished surfaces were perfectly adapted to X-ray analyses, hence, it was possible to study the same set of polished cross-sections with a wide set of micro-imaging techniques: visible, electron, X-rays and infrared microscopes as well as ToF-SIMS. Besides, these samples were very precious, tiny and their stratigraphy was not always visible under light observation. Hence, it would have been very difficult to pre-
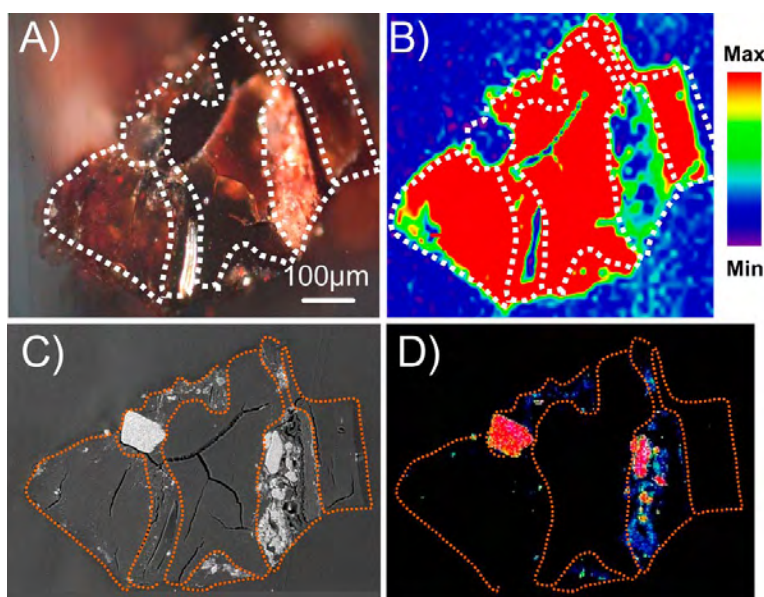
Figure 2: Analysis of a polished section of a fragment taken from the patina of African statues (ref 71.1935.60.332) by a combination of micro-imaging techniques: A) visible microscopy, B) SR µFTIR: distribution of proteins, C) electron microscopy, BSE mode, D) SEM/EDX: distribution of silicon.

pare different samples for the different techniques and consequently to correlate data. In this specific case, the preparation of single, versatile samples was clearly rewarding. Figure 2 gives an example of results, in which a successive distribution of proteinaceous and inorganic layers is observed. Such chemical mappings provide images of possible successive libations of the statues during ritual ceremonies.[7-8]

Even if thin sections are more appropriate, µXRD can also be carried out on polished sections, either in "reflection" mode: the surface is almost tangential to the beam; or in "transmission" mode: the sample can be placed orthogonal to the beam, the beam crosses the sample and the embedding resin. A scheme of the different configurations can be found elsewhere.[9] In the transmission mode, the resin may interfere in the diffraction patterns. Its contribution can be subtracted before data treatment. As an example, N. Salvadó et al. studied some copper-based green pigments in Jaume Huguet's gothic altarpieces, by combining µXRD on polished sections, and FTIR on small particles placed in a diamond cell.[10] More recently, the same approach was followed for the full identification of pigments, binders, supports, and reaction and weathering compounds in Romanesque wall paintings from the church of Saint Eul'alia of Unha (central Pyrenees).[11]

2.3 Preparation and analysis of thin sections

As mentioned before, working in transmission on thin sections can be highly useful, not only for µFTIR but also for µXRD or µXANES. Accordingly, even if it is

particularly tricky in the case of paintings, preparing thin sections can be very worthwhile. A diamond knife is usually requested to slice painting fragments, which can be composed of both soft binders and hard pigments. The optimal thickness is not the same for the different analytical techniques. For µFTIR, the thickness should not exceed 4-5 µm, to avoid saturation of the most intense vibration modes. For µXRD, thicknesses ranging from 30 to 200 µm are acceptable, depending on sample composition, and beam energy. While one wants to combine µFTIR and µXRD on the same object and succeeds to prepare thin sections, it is relatively easy to slice two consecutive sections, of two thicknesses, and then to prepare samples adapted to each instrument. Such an approach was adopted to study the weathering of gilding decorations in the case of Sant Benet de Bages (Barcelona, Spain). The crossed identification of calcium oxalates and organic materials was done by combining µFTIR and µXRD.[12] In a similar experiment, µFTIR and powder X-ray diffraction were carried to identify both organic and inorganic constituents of ancient varnishes covering music instruments. 2D FTIR mappings were acquired on 5 µm-thick sections, with a 10 µm-beam, while X-ray diffraction patterns were obtained on raw varnish fragments with a 300 µm-beam. In particular, a mixture of proteinaceous binders and of calcium sulphates was evident.[13]

These two publications reported the intricacy of preparing thin sections.[12-13] In the case of Spanish paintings, the authors underline problems encountered due to the possible presence and interference of embedding resin inside the sample. The embedding resin did not prevent the localization of oxalates, which was the major objective of the study, but it hampered the clear identification of organic compounds. To overcome this difficulty, different strategies have been proposed.

One way consists in replacing the absorbing organic resin with a transparent inorganic matrix, usually KBr. Two main approaches are described: either the preparation of a polished section,[14] or the preparation of a thin section by polishing the two sides of a KBr pellet in which the sample is placed.[15] The second strategy was followed to analyze protrusions present in anonymous portrait made on canvas, dating from 1610 and conserved in the Musée du Chatillonais, France (Nº inv. 15).[16] Such aggregates grow inside paintings and may damage it by creating kinds of small volcanoes. They remained mysterious for a long time until they were identified as aggregates of metal carboxylates, usually lead soaps. In the present

study, µFTIR clearly confirmed the presence of spots of carboxylates within a ground layer made of partially saponified oil and ochre (Fig. 3). µXRF assessed the identification of lead in protrusions. Besides, µXANES was performed to estimate lead speciation, with the aim to evaluate the oxidation state of lead. Figure 3H presents the distribution of Br. Its presence around the sample does not alter neither µFTIR nor µXRF experiments. Conversely, the KBr layer, present behind the sample to give more stability to the pellet and to enable its handling when polishing, has two disadvantages: first, for µFTIR analysis, it may slightly distort the beam path, hence altering the alignment; second, at the lead M-edges (~2.5 keV), it impedes the measurements of transmitted beam. XANES spectra must be collected in fluorescence.

This sample preparation has two other critical drawbacks: it is difficult to obtain a homogeneous thickness over the sample by double polishing, and above all, the final polishing can end in a complete loss of the sample. For this reason, a second methodological approach was preferred for the analysis of a painting fac-simile, prepared with respect to the ingredients identified in the ancient anonymous portrait. Only one month after painting it, protrusions were detected at the surface of the fac-simile. For their analysis, the same analytical strategy, combining µFTIR, µXRF and µXANES, was followed. But conversely, sample preparation was modified. As polishing turned out to be fastidious and critical, obtaining thin sections with a microtome was chosen. Unfortunately, without any protection, the embedding resin diffuses inside the sample, and may complicate FTIR data analysis. To create a barrier between the embedding resin and the sample, the painting fragment was first wrapped into an aluminium foil. Then, the set was placed in an embedding resin and slices of 5 µm were obtained with a microtome. This approach was facilitated both by the relative flexibility of the "fresh" painting, and by its low preciousness. Indeed, it was possible to cut a 6 mm^3-fragment to enable easier handling and positioning. The same sample preparation has not been yet tested on tiny, precious ancient paintings but it perfectly worked on fragments of ancient mummy skins.[17] Figure 4 presents some elemental and molecular images obtained on such a section. In the visible image (Fig. 4A), the remaining aluminium foil
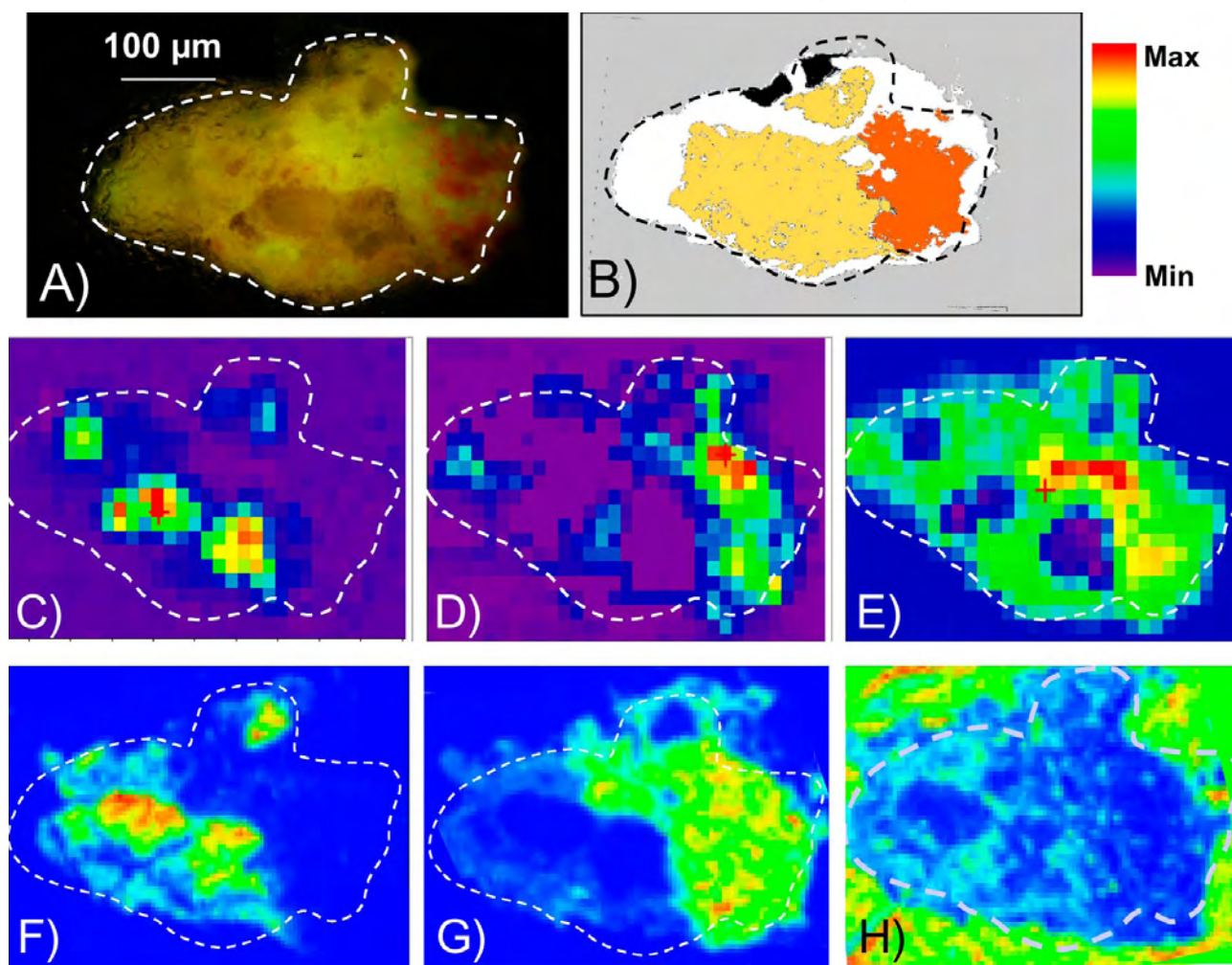

Figure 3: Analysis of a double-face polished section of a painting fragment, embedded in KBr, by a combination of µFTIR (C to E) and µXRF (F to H): visible microscopy A), scheme representing the three main layers: yellow = ground layer, orange = protrusion, black= colored layer B), molecular distributions of quartz C) carboxylates D) and esters E), elemental distributions of silicon F), lead G) and bromine H).
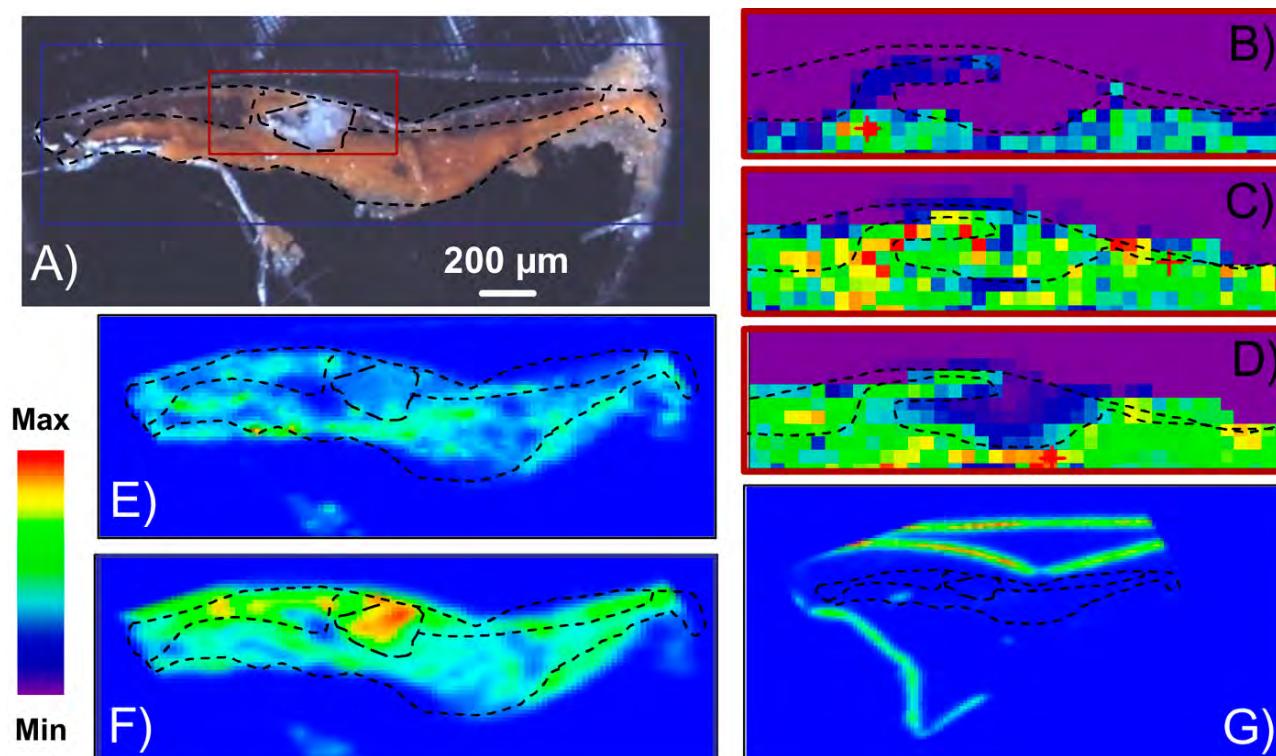
Figure 4: Analysis of a thin section of a painting fragment, wrapped in aluminium, embedded in resin and cut with a microtome, by a combination of µFTIR (red rectangle, B to D) and µXRF (blue rectangle, E to G): visible microscopy A), molecular distributions of kaolinite B) carboxylates C) and esters D), elemental distributions of silicon E), lead F) and aluminium G).

and embedding resin are still visible. Figures 4C and F confirm that the white protrusion is made of lead soap. Figure 4G shows the distribution of aluminium foil which did fulfil its function of barrier between resin and sample. XANES spectra were simultaneously collected in fluorescence and transmission modes, and it appears that slice thickness, which was originally chosen for FTIR acquisitions, was perfectly relevant for µXANES. A complete description of results can be found elsewhere.[16]
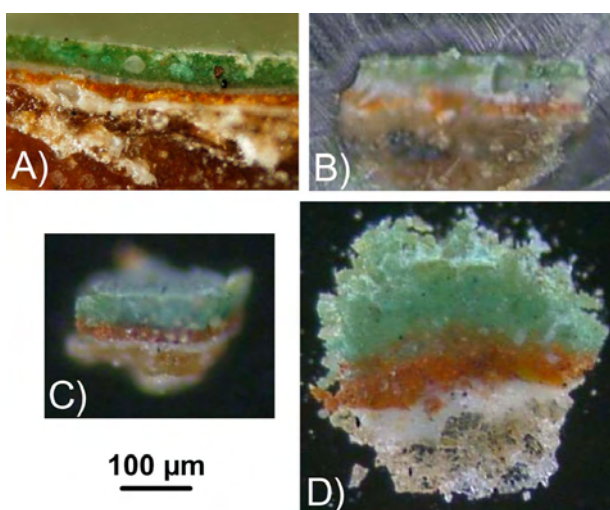

Figure 5: Different sample preparations performed on fragments of the same painting (Foladi, FDM55). Polished, in resin A), cut, in resin B) raw, before C) and after D) compression in diamond micro-compression cell.

2.4 Preparation and analysis of pressed sections

Protecting sample with a foil can become particularly arduous in the case of tiny fragments. Besides, once wrapped, it may be difficult to orientate the sample properly, to cut it transversally to the painting surface. Another way to prevent the interfering presence of embedding resin consists of not embedding the sample at all, and working on raw fragments. Usually, these fragments are too thick to be studied in transmission directly. Diamond micro-compression cells are devices specially used to thin and flatten samples for FTIR analysis. As an example, they were used for the analysis of fragments from Jaume Huguet's altarpieces,[10] Romanesque wall paintings,[11] as well as Egyptian cosmetics.[18] This method has the advantage to avoid contamination of any exogenous compounds. In the case of paintings, its use can be improved by paying a special attention to the positioning of fragment before pressing. Indeed, by using small fragments and by placing them orthogonal to the diamond window, the painting stratigraphy can be preserved, being only slightly distorted but also enlarged. This method was applied to a set of about twenty painting fragments, from Bamiyan, Foladi and Kakrak, ancient Buddhist sites located in the highlands of Afghanistan. As these paintings were suspected to contain complex mixtures of organic and mineral compounds, a combined analysis by µFTIR and µXRF/µXRD was planned. Originally, it was
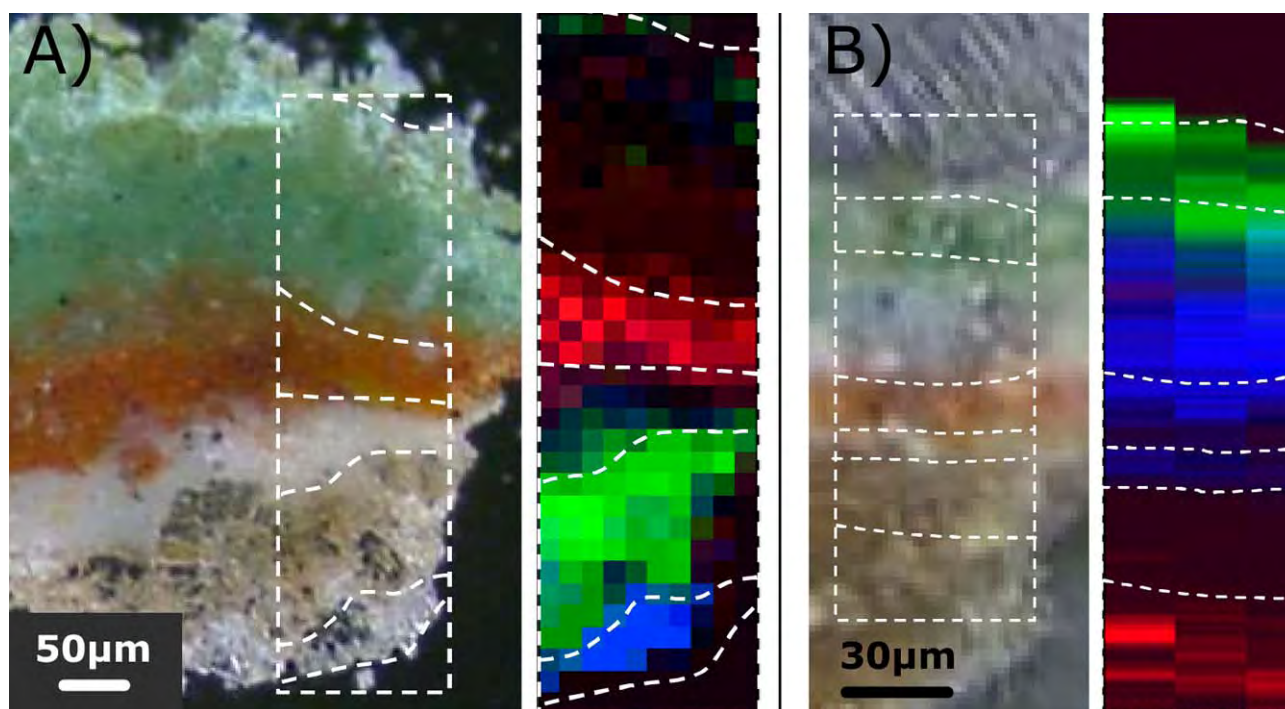
Figure 6: Visible light picture and chemical mapping on a fragment of the Buddhist painting (Foladi, FDM55). µFTIR: molecular mappings of goethite (red), polysaccharides (green) and resin (blue) A), µXRF/µXRD: phase and elemental mappings of quartz (red), copper (green) and hydrocerussite (blue) B).

expected to work on thin sections, obtained with a microtome, of about 5 µm for µFTIR and about 30 µm for X-ray analyses. These sections were appropriate for X-ray acquisitions, but it turned out that the presence of embedding resin was a disaster for infrared analysis. It was almost impossible to identify original organic materials in thin sections. It was then decided to prepare adapted samples for µFTIR with micro-compression cells. Figure 5 shows three fragments of the same painting prepared by i) embedding in resin and polishing (Fig.5A), ii) embedding in resin and cutting with a microtome (Fig. 5B), iii) compression with a diamond micro-compression cell (before: Fig. 5C; after: Fig. 5D). Some images obtained with µFTIR are given in Figure 6, but more results obtained by µFTIR, µXRD and µXRF mappings on this painting are presented elsewhere.[3-19]

For a successful preparation, the sample is pressed only when it is positioned perpendicular to the diamond window, which is the most delicate part of this preparation. In some cases, it was possible to remove the sample entirely from the diamond window and to place it on a ZnS window, which is less absorbent in the mid-infrared domain.

For another analysis (unpublished results), the painting fragment, still stuck on the diamond window, was analysed by µXRF. It showed that the diamond window was fully compatible for micro X-ray analyses in fluorescence.

With the example of Bamiyan paintings, it appeared that it was more interesting to prepare appropriate samples for each technique, instead of a single versatile but finally useless sample. Adapted ways of preparation must be favoured when i) there is enough material to prepare several samples, ii) the stratigraphy is sufficiently clear to be observed with a visible microscope; in other words, visible images will enable to link the various chemical images. Concerning sample preparation (polished, cut, pressed…), the strategy must be adapted to the sample properties (hardness, brittleness…), to the requirements of the analytical instruments and to the scientific questions.

3 Data treatment: versatile vs. customized software packages

Sample preparation is a challenging step before the experiments. After the experiment data treatment can be equally demanding, in particular in the case of a combination of different techniques. Each instrument is usually associated with a specific data format, dedicated software and a database which are often incompatible. Even if the chemical information contained in the data is totally different, the raw format of µXRF, µXANES, µXRD, µFTIR but also SEM/EDX, µRaman, ToF-SIMS 2D-mappings are quite similar. For all these techniques, hyper-spectral data are generated with a 3D matrix, containing a fluorescence spectrum, a XANES spectrum, a diffraction pattern (the 2D rings can be integrated into a 1D profile), an infrared spectrum, a fluorescence spectrum, a

Raman spectrum or a mass spectrum, respectively, for each pixel. Even if adapted software packages are more relevant for a precise interpretation of data, the basic manipulation of these hyper-spectral data requires the same tools: the possibility to map bands intensity (often called ROI for "region of interest"), in order to generate elemental, molecular or phase images; and conversely the possibility to calculate the average spectrum over a precise region of the sample.

PyMCA is freely downloadable software originally developed to process X-ray fluorescence data, in particular to decompose fluorescence signals into various contributions of various emission lines of various elements.[20] Particular attention was paid to reduce the time requested for each fit, in order to manage the fit of thousands of spectra in a reasonable time. A batch process is offered to generate elemental mappings. In parallel to this dedicated mode for fluorescence treatment, a more basic mode was developed for the easy handling of 2D-maps of 1D data (ROI imaging). It provides the two previous options described previously (generation of ROI mappings, sum/average spectra), and it offers also a useful RGB visualisation that enables an easy superimposition of images. Following the growing number of experiments combining μXRF with μXRD or μFTIR, implementations were done to handle μXRD and μFTIR data. The only proprietary μFTIR format currently supported as input is the Nicolet .MAP data generated with OMNIC 7.3 but other formats can be implemented if they are properly described and/or the necessary software provided. Current PyMCA (version 4.3.0) also implements principal components analysis (PCA) as a complementary imaging technique.

As an example, Figure 6A presents the RGB superimposition of three vibrational bands, characteristic of goethite, polysaccharides and resin. In the case of combining μXRF and μXRD, generated maps have usually the same dimension (pixel and map size), since fluorescence and diffraction signal are generally collected simultaneously. In such configurations, PyMCA offers a combined handling of data; thus, elemental and phase mappings can be directly superimposed. Accordingly, a synergetic treatment of the two sets of data can be realized. In Figure 6B, phase (quartz and hydrocerussite) and elemental (copper) mappings are superimposed.

4   Conclusion

FTIR is a method of paramount importance for the study of ancient paintings. The development of FTIR microscopy was a decisive step that completed the compounds identification with geographical information. Synchrotron sources significantly improve the method by offering a high lateral resolution. The major difficulty for the study of painting fragments by μFTIR, with a synchrotron source as well as with a Globar source is the sample preparation. The most classical method which consists in embedding the fragment in resin and polishing it is rarely the best solution. Several strategies were explored, with the motivation to perform μFTIR analyses in transmission. In parallel, developing a multi-modal study of the samples by combining X-ray with infrared analyses can be particularly rewarding as it offers complementary elemental and structural information at the micrometer scale. Here again, sample preparation has to be considered. Depending on the case (sample size, visible/invisible structure, etc.), a single or several adapted samples could be prepared. There is clearly no unique solution, and appropriate strategies must be developed for each situation. Concerning data treatment, the development of versatile software packages such as PyMCA can be useful for handling and processing various sets of hyper-spectral data.

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