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Recent applications and current trends in Cultural Heritage Science using synchrotron-based Fourier transform infrared micro-spectroscopy

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Abstract

Synchrotron-based Fourier transform infrared micro-spectroscopy (SR-FTIR) is one of the emerging techniques increasingly employed for Cultural Heritage analytical science. Such a technique combines the assets of FTIR spectroscopy (namely, the identification of molecular groups in various environments: organic/inorganic, crystallized/amorphous, solid/liquid/gas), with the extra potential of chemical imaging (localization of components + easier data treatment thanks to geographical correlations) and the properties of the synchrotron source (namely, high brightness, offering high data quality even with reduced dwell time and reduced spot size).

This technique can be applied to nearly all kind of materials found in museum objects, going from hard materials, like metals, to soft materials, like paper, and passing through hybrid materials such as paintings and bones. The purpose is usually the identification of complex compositions in tiny, heterogeneous samples.

Recent applications are reviewed in this article, together with the fundamental aspects of the infrared synchrotron source which are leading to such improvements in analytical capabilities. A recent example from the ancient Buddhist paintings from Bamiyan is detailed. Emphasis is made on the true potential offered at such large scale facilities in combining SR-FTIR microscopy with other synchrotron-based micro-imaging techniques. ***To cite this article: M. Cotte et al., C. R. Physique 10 (2009).***

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Résumé

Applications récentes et tendances actuelles dans l'analyse des matériaux du Patrimoine par spectroscopie infrarouge à transformée de Fourier sur installation synchrotron. La spectroscopie infrarouge par transformée de Fourier sur installation synchrotron (SR-FTIR) est de plus en plus utilisée pour l'analyse d'objets du patrimoine culturel. Cette technique combine

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les avantages de la spectroscopie FTIR classique (notamment l'identification de groupes moléculaires dans des environnements divers : organique/inorganique, cristallisé/amorphe, solide/liquide/gaz), avec les atouts de l'imagerie chimique (localisation des composantes + un traitement des données facilité grâce aux corrélations géographiques) et les propriétés des faisceaux synchrotrons (en particulier, la brillance qui permet d'obtenir des données de grande qualité, même avec des temps d'acquisition et des tailles de faisceau réduits).

Cette technique peut être appliquée à une majorité de matériaux constitutifs des objets de musée : des matériaux durs, comme les métaux, aux matériaux mous, comme les papiers, en passant par des matériaux hybrides comme les peintures ou les os… L'objectif est généralement d'identifier des compositions complexes dans des échantillons minuscules et hétérogènes.

Cet article aborde quelques aspects fondamentaux de la spectroscopie infrarouge sur source synchrotron. Une revue des applications récentes illustre les potentialités de la technique. Un exemple récent d'étude de peintures bouddhiques de Bamiyan est détaillé. La combinaison de la micro-spectroscopie infrarouge avec d'autres techniques de micro-imagerie sur synchrotron est également soulignée comme une valeur ajoutée de notre approche. ***Pour citer cet article : M. Cotte et al., C. R. Physique 10 (2009).***

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Mots-clés : Synchrotron ; Infrarouge ; IRTF ; IR-TF ; Héritage culturel ; Peinture ; Ancien

1. Introduction

This article aims at providing a deeper understanding of the new capabilities offered by synchrotron radiation (SR) infrared (IR) emission in the field of Cultural Heritage (CH) analytical science. The synchrotron source is providing about two orders of magnitude higher brightness (or brilliance) compared to a thermal (laboratory-based) source. The principal motivation for synchrotron-based IR micro-spectroscopy is to achieve significantly greater lateral resolution (typically close to the diffraction limit) in combination with superior signal-to-noise ratio without resorting to prohibitively long acquisition times. This advantage has been widely exploited in several synchrotron facilities worldwide, with a number of major achievements in a variety of scientific disciplines: soft matter [1–3], geology [4], biology [5–10]. The increasing demand for beamtime by the various communities, including Archaeology and Cultural Heritage ones, has resulted in an expansion of the synchrotron IR beamlines throughout the world. Active SR-FTIR micro-spectroscopy beamlines are found worldwide:

- in North America, at the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory) presently operating six IR beamlines, with four SR-FTIR microscopes (Beamlines U2A, U2B, U4IR, and U10B), ALS, Berkeley, SRC, Stoughton, Duke-FEL, Durham (USA); CLS, Saskatoon (Canada);
- in Asia: at UVSOR, Okasaki and SPring8, Nishi-Harima (Japan); NSRRC, Hsinchu (Taiwan);
- in Australia: at the Australian Synchrotron, Melbourne (Australia);
- and in Europe: at the ESRF, Grenoble (France), SOLEIL, Gif sur Yvette (France), ELETTRA, Trieste (Italy), SLS, Zurich (Switzerland), ANKA, Karlsruhe (Germany); BESSY II, Berlin (Germany), MAXLAB, Lund (Sweden), whereas a new IR beamline will open soon at Diamond, Rutherford Lab (UK).

Although most IR microscopy imaging makes use of the rich and unique spectroscopic absorption features found in the mid-IR for chemical identification, there is an increasing interest in extending the spectral range to lower frequencies. This evolution is motivated in part by developments in coherent THz spectroscopy and imaging [11], but also in response to the needs of the Space sciences community for the identification of complex minerals found in interplanetary dust particles [12]. The broad spectral coverage and high brightness of synchrotron radiation (SR) reaches well into the far infrared, to below 1 THz [13]. It is foreseen that such a development will be of great benefit in Cultural Heritage Science.

The purpose of this article is to address how synchrotron infrared emission has been combined with the existing spectrometer + microscope instruments to advance infrared spectroscopic imaging in ways that would prove quite difficult with a conventional thermal source. To address this question, we will detail the nature of the synchrotron infrared source, the optical performance of the micro-spectroscopy instrument. We will begin our review with a description of source power, source brightness (or spectral radiance, or brilliance), intensity distribution at the detector, and dependency with wavelength, for both the synchrotron and blackbody (thermal) sources. We will then discuss diffraction and how it affects the image resolution and contrast for a typical infrared micro-spectrometer system. This will lead

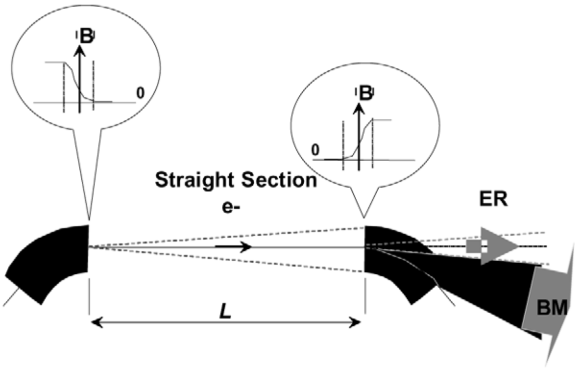

Fig. 1. Schematic drawing of the infrared emission from edge radiation (ER) and bending magnet radiation (BM). L is the length of the straight section, and this influences the interference effects with the upstream ER dipole emission.

us to show how such properties have been exploited in Cultural Heritage Science, and how we foresee the expansion of such analytical capabilities, by combining with other synchrotron based-microscopic techniques available at such facilities.

2. Synchrotron infrared emission

2.1. The making of synchrotron light

Electron-based synchrotron light sources use magnetic fields to bend the electron trajectory into a closed orbit. SR is produced at each of these "bending" magnets. The emitted radiation spans an extremely broad spectral domain, extending from the X-ray regime to the very far IR region. IR radiation is generated by electrons traveling at relativistic velocities, either in a curved path through a constant magnetic field (i.e. bending magnet (BM) radiation [14]) or when their trajectories encounter variable magnetic fields, e.g. at the edges of BM (i.e. edge radiation (ER)) (Fig. 1).

In the latter, less-common case, the edge radiation is generated by a high-energy charged particle when it encounters a rapid change in magnetic field either at the entrance, or at an exit of a bending magnet. For this reason, photons are produced not only at the end of a straight section, but also at the beginning of the straight section. Accordingly, interferences between the emitted photons occurs, resulting in a "donut-like" line shape of the emission pattern, which manifests itself in oscillations of radiation intensity [15,16].

Flux and brightness for the two types of IR emission are almost equivalent, but the opening angle of the ER is narrower than that of the SR from constant field of a BM. The intensity profiles of the two types of emission are also different, and depend upon wavelength. In Fig. 2, the distribution profiles at two wavelengths (10 μm and 100 μm) have been calculated for a medium energy storage ring (3.0 GeV) for a prototypical opening angle of the dipole chamber of 20 × 40 mrad (vertical by horizontal) for the collection of BM infrared emission, and 20 × 20 mrad for the collection of the ER infrared emission. These profiles illustrate that, for BM emission, the angle of emission is larger than that of the ER. However, flux and brightness are equivalent for the two types of emission sources, and either one can be used for synchrotron infrared experiments.

This has some advantages for engineering purposes, since the dipole chamber exit port in a synchrotron storage ring has to be enlarged for BM radiation. Thus today, both sources are used for extraction, depending upon availability of a straight section and/or BM. The most recent synchrotron facilities are collecting both sources, and split them after the propagation to the instrument in order to have two spectroscopic branches with the same extraction port (Australian Synchrotron, SOLEIL, Diamond).

A marked difference between the two sources is their polarization properties. BM emission is strictly horizontally polarized in the plane of the electron trajectory, while ER has a radial polarization.

2.2. Flux versus brightness

The brightness of synchrotron light is defined as the photon flux or power emitted per source area and solid angle. Most of the experiments in SR-IR spectroscopy exploit the brightness advantage of the source, while the flux advan-

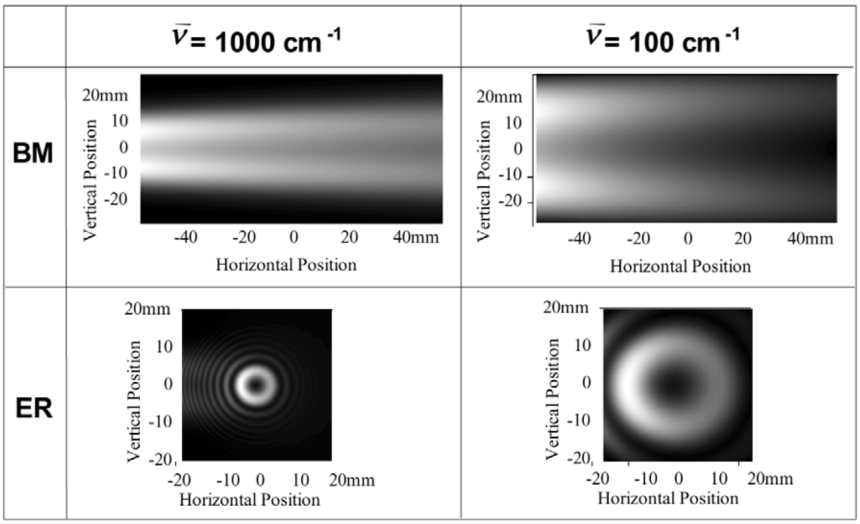

Fig. 2. Intensity distribution of edge radiation, for two wavelengths: λ = 10 μm (left column) and λ = 100 μm (right column). The distribution has been calculated for a bending magnet (BM) emission, and an edge radiation (ER) emission. This calculation has been carried out for the case of a storage ring of 3 GeV, and a vertical aperture of 20 mrad.

tage is exploited mainly in the far IR region. It is important to note that SR does not provide a much higher photon flux than a conventional IR source (such as a globar), unlike the traditional case in the X-ray region. In fact, the total flux can be much less (about one to two orders of magnitude) in the mid IR region, although it becomes superior at long wavelengths [17].

The crucial factor is that the effective synchrotron source size is quite small, i.e. on the order of ∼100 μm or less for newer synchrotron storage rings. Also, the light is emitted into a narrow range of angles due to SR characteristic, and the resulting brightness is vastly increased.

The apparent brightness of SR can be 2–3 orders of magnitude higher than that of a globar source [17]. However, it is interesting to note that, contrary to X-ray irradiation, sample heating is negligible, permitting analysis of single cells for time scales from hours to days [18].

2.3. Lateral resolution

When considering the available spatial resolution, two parameters must be considered. The first is the acceptable signal-to-noise (S/N). The flux – and thus S/N – decreases drastically as apertures in the IR microscope are reduced to confine the IR beam to smaller areas. The second issue is diffraction (residual optical aberrations of the focusing optical elements are neglected). The resolution issue has been evaluated both theoretically and experimentally by G.L. Carr [19]. With the use of a synchrotron source, the diffraction limit is achieved when the microscope's apertures define a region with dimensions equal to the wavelength of interest. However, the use of a confocal optical arrangement leads to a 30% improvement in spatial resolution, in agreement with the diffraction theory [19].

3. Infrared beamlines and microscopes

3.1. Beamlines

Extraction of the synchrotron light from a synchrotron storage ring is generally accomplished with a combination of gold- or aluminum-coated plane and toroid/ellipsoid or spherical mirrors.

In most of the existing SR-FTIR beamlines, the first mirror is flat and deviates the beam either vertically or horizontally to the first focusing mirror. This "extraction" mirror must be able to handle the heat load of higher energy photons (i.e. x-rays); so water-cooling, water-cooled masks, and/or slotted mirrors are employed. Combinations of focusing and flat mirrors are then used to transport the beam outside the shield wall of the storage ring.

The IR light is then focused through an IR-transparent window (usually diamond, but in a few cases IR-transparent windows such as KBr, ZnSe and KRS5 have been used), which separates the ultra-high vacuum (UHV) conditions of the storage ring (10^{-9}–10^{-10} mbar) and the low vacuum of the SR-FTIR beamline (10^{-3}–10^{-4} mbar). This diamond window is usually a slight wedge shape to avoid interferences, and relatively small in diameter (10 to 40 mm clear aperture). Some sophisticated wheels containing windows of several materials (e.g. calcium fluoride, diamond, cesium iodide) have been recently implemented at the Swiss Light Source for the same purpose.

The low vacuum section of a SR-FTIR beamline is generally terminated with an IR-transparent window (KBr, CsI, polyethylene) either after a vacuum-based FTIR spectrometer or prior to a purged instrument. This window isolates the beamline vacuum from the ambient pressure of the spectrometer and/or microscope. To date, all commercial FTIR microscopes operate at ambient pressure and are typically purged with dry N_2 or dry air to remove any water vapor and carbon dioxide in the FTIR spectrum.

3.2. *Infrared microscopes and spatial resolution*

FTIR microscopes are commercially available from a number of companies worldwide. In recent years, these microscopes have been improved so that they now include many of the features of research-grade optical microscopes such as polarization, Nomarski measurements, Difference Interference Contrast (DIC), and epifluorescence. They are also equipped with sophisticated software packages for generating and analyzing chemical images.

The microscope uses reflecting Schwarzschild-type objectives to avoid absorption and chromatic aberrations over the large mid-IR spectral range. One objective serves to focus the light onto the specimen, while the other collects the light and relays it towards the detector. An aperture is used to constrain the illuminated and detected areas on the sample. The spatial resolution is in practice limited by the wavelengths of IR light, which are longer than visible light wavelengths used for conventional optical microscopy. The diffraction-limited spatial resolution scales with the wavelength of light and the numerical aperture (NA) of the focusing optic [20]. Typical FTIR microscopes utilize Schwarzschild objectives with a NA of ~ 0.6. Some microscopes rely on a single aperture before the sample, which controls the region illuminated. With a single aperture, the diffraction-limited spatial resolution is approximately $2\lambda/3$ [19]. Thus for the mid-IR range, the diffraction-limited spatial resolution is approximately 1.7 μm (at 4000 cm^{-1}) to 13 μm (at 500 cm^{-1}). Other microscopes operate in a confocal arrangement, where a second aperture is used after the sample to define the region being sensed by the IR detector. For such a confocal microscope, the spatial resolution is improved to $\sim\lambda/2$ [19]. In addition, the confocal arrangement also reduces the Schwarzschild's first- and higher-order diffraction rings, dramatically improving image contrast [19].

To date, most synchrotron-based infrared microscopes operate in a confocal (i.e. dual-aperture) arrangement and utilize a single-element IR detector. For these microscopes, very few modifications are needed to convert a commercial instrument into a synchrotron infrared based microscope.

3.3. *Confocal geometry and contrast fidelity*

In the field of Cultural Heritage, materials are usually complex and heterogeneous. In this respect, FTIR analyses benefit greatly from high quality data collected at high spatial resolution. As such, domain sizes close to the diffraction limit are important and blurring effects can distort the spectroscopic information. Since this aspect is a fundamental advantage of the infrared synchrotron source, the following illustrates the importance of preserving the contrast fidelity.

As an example of the importance of a confocal geometry, Fig. 3 shows a ring-shaped test pattern with a 14 μm ring diameter and a thickness of 2 μm. The center and right images represent the calculated chemical image with a 6 μm wavelength for a single aperture (non-confocal geometry) and two apertures (confocal geometry), respectively. It is very clear that, for the non-confocal geometry, one may conclude that there is a chemical component with a characteristic frequency at 6 μm. This shows that an artifact can be introduced in the case of high resolution.

3.4. *Spectral quality improvements using synchrotron infrared microscopy*

In order to illustrate the superior spectral quality (e.g. higher signal to noise), while importantly preserving the contrast fidelity (thanks to confocal geometry), we have compared the spectra obtained on a single prototypical biological

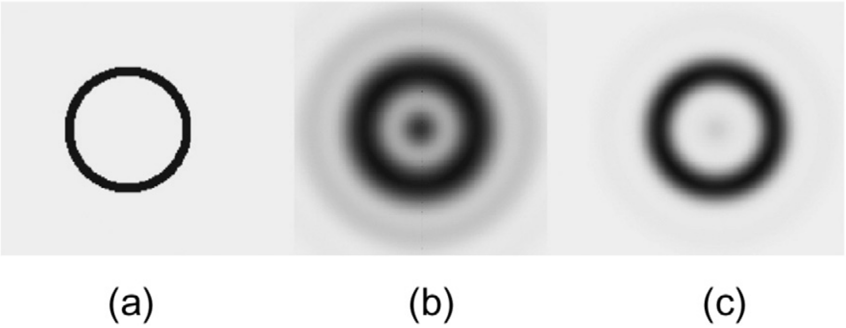

Fig. 3. Calculated images for a 14 µm diameter ring-shaped object at $\lambda = 6$ µm. (a) Actual object; (b) image for a (single aperture) non-confocal 32× Schwarzschild objective with $NA = 0.65$; (c) image for a confocal (dual aperture) 32× Schwarzschild objective with $NA = 0.65$. (From [17].)

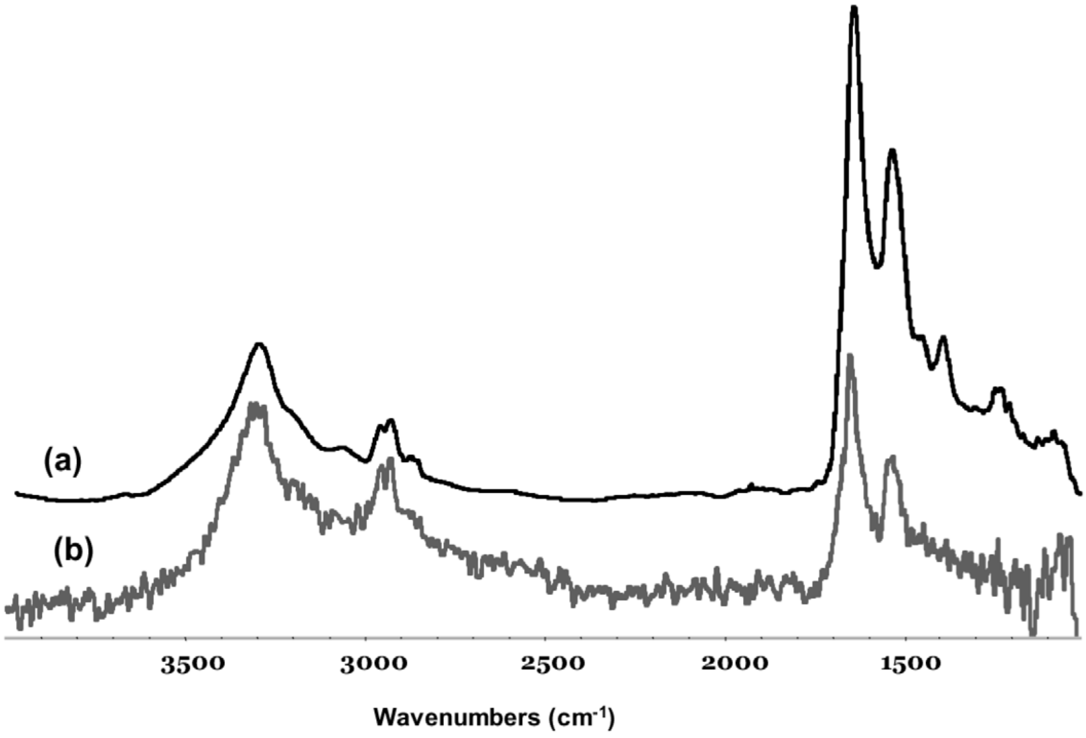

Fig. 4. FTIR spectra recorded with a dual aperture of 6×6 µm^2, at 4 cm^{-1} resolution, derived from a sum of 128 scans with (a) the synchrotron source and (b) with the internal (globar) source.

cell (HELA cell – from brain cell line), using either the synchrotron beam, or the internal source, with an aperture of 6×6 µm^2, corresponding roughly to the size of the nucleus of this type of cell specimen (Fig. 4).

4. Applications in the field of Cultural Heritage

The potential of vibrational spectroscopic techniques (mainly FTIR and Raman spectroscopies) for the study of ancient compounds is now well established [21]. These techniques offer clear assets to tackle the experimental challenges associated with the analysis of Cultural Heritage objects (mainly preciousness, chemical complexity, heterogeneity). These two techniques can probe both organic and inorganic species, and appear to be rather complementary to each other. Unlike Raman microscopy where using laser illumination damage can sometimes be observed, FTIR microscopy does not induce any sample damage.

In addition to point identification, the raster scanning of the sample under study allows establishing a two-dimensional map which helps determining the distribution of molecular groups, and also to more precisely identify the various component's location. It is well recognized, nowadays, that the two vibrational techniques (Raman and Infrared) are increasingly popular in Museums and associated scientific institutes.

Biologists were the first community to exhibit a strong demand for analysis at the diffraction limited resolution, afforded by the SR-FTIR microscopes. Very soon after, Cultural Heritage (CH) scientists promptly realized the potential of such instruments (improved data quality, signal to noise ratio, dwell time and lateral resolution).

A first exposition to the CH community was done in 2003, through the Journal of the American Institute of Conservation [22]. Since then, the number of applications of SR-FTIR is continuously increasing.

Two different measurement set-ups are usually employed. On one hand, the analyses can be carried out at the surface of entire objects, without any sampling. As an example, this approach has been employed for the direct characterization of bronze corrosion [23]. To enable reflectance spectra to be collected from large samples, a side port accessory is necessary to direct the infrared beam sideways from the microscope onto the sample.

On the other hand, and indeed in most of the cases, analyses have been performed on micro-fragments. The wide range of chemicals probed by FTIR explains the variety of applications. Some studies are specifically focused on the identification of organic compounds (e.g. resinous materials used in water proofing in ancient Iberian amphora [24]; organic coating on historical 18th and 19th C furnitures [25]). Other studies deal with the identification of inorganic compounds (e.g. corrosion compounds on bronze objects [26]). But, more generally, samples studied with SR-FTIR are hybrid complex materials. SR-FTIR sensitivity is then fully exploited. Multi-layered paintings are typical specimens benefiting from SR-FTIR capacities: simultaneous identification of organic materials (binders, mordants, varnishes, glazes as well as some organic pigments), of inorganic materials (pigments, fillers) but also of hybrid materials (usually carboxylates, resulting from the reaction of organic ingredients with inorganic compounds) [23,27–31].

Similar hybrid formulations were studied in various contexts: in ancient cosmetics [32], the patina of African statues [33], or in the varnish covering ancient music instruments [34]. In all these cases, the sample complexity may result from both an intricate deliberate formulation by the artist or the craftsman plus some ulterior unintentional alteration reactions. The possibility to probe at the micrometer scale, the majority of these constituents is a clear asset for the complete elucidation of ancient formulation practices as well as the better understanding of degradation phenomena.

In other cases, e.g. ancient biological tissues, the heterogeneity is intrinsic to the sample. Here again, alterations will make the chemical composition even more complex with the possible bio mineralization producing hybrid materials. Comparison between fresh and ancient tissues enables identification of decay markers. Thanks to 2D imaging, these markers can be scanned over the whole tissue structure showing for example that, in skin, the outmost layers are far from being the most degraded [35].

To illustrate the variety of information that can be obtained with SR-FTIR, Fig. 5 shows an application for the analysis of a painting fragment. This micro fragment (BMM35) was part of a wall painting in cave N(a), in the Bamiyan site, Afghanistan. It was taken in the context of a wide conservation project as well as historical and technical study of Buddhist painting techniques, around 5th–9th centuries, funded by the UNESCO/Japanese Funds-in-Trust [36].

These paintings have revealed highly complex composition and sophisticated technology. The palette of ingredients was very wide, not only for pigments but also for organic materials. They were mixed and applied as multi-layer structures, leading to refined optical effects. Oil in particular was identified, shedding a completely new light on historical development of oil paintings [30,37].

Fig. 5A shows the sample structure, from the top: 1 = yellowish transparent layer, 2 = green layer, 3 = black layer, 4 = white ground, 5 = transparent brownish layer, and earthen rendering. The complete study of this sample is detailed elsewhere [38]. Average spectra obtained in layer 2, 4 and 5 are given in Fig. 5C. Fig. 5B shows three examples of ingredients (1 organic, 1 hybrid, and 1 inorganic) identified, and localized by SR-FTIR: in red, the protein-based sizing/sealing (probed by the characteristic amide I band, at $\sim 1650\ \text{cm}^{-1}$), restricted to layer 5. It can indicate the use of either egg white or animal glue. In green, carboxylates (probed by the C=O stretching around $1550\ \text{cm}^{-1}$), resulting from the reaction of oil esters with some inorganic compounds. In this case, a mixture of lead and copper soaps is suspected, particularly in the green layer. In blue, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), probed by the characteristic OH stretching at $3534\ \text{cm}^{-1}$. It is one of the lead carbonates entering into lead white composition. It is highly concentrated in the white layer (#4), but also present in the green one (#2).

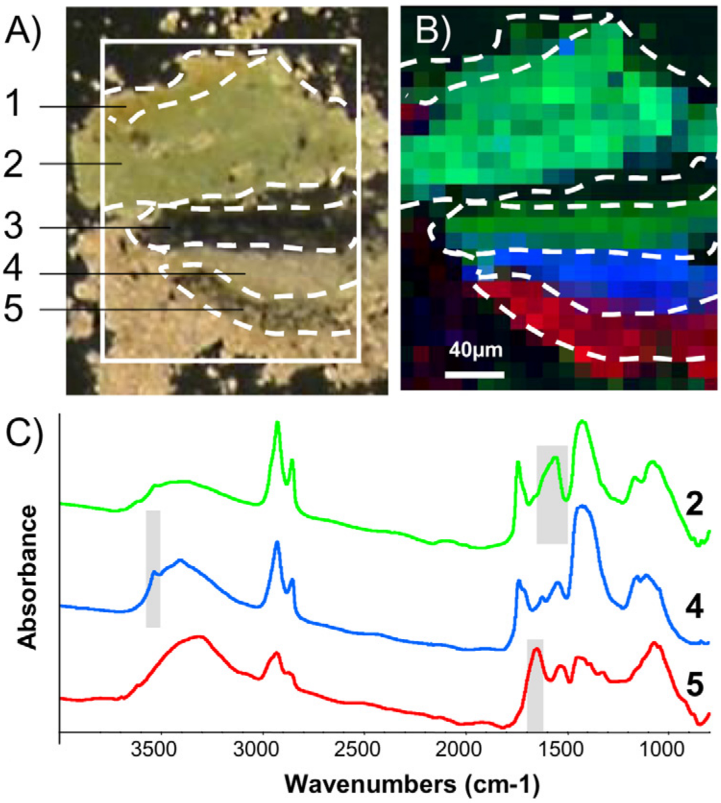

Fig. 5. A) Photomicrograph of pressed fragment of sample BMM035 from Cave N(a), Bamiyan, showing a multi-layered structure: 1 = yellowish transparent layer, 2 = green layer, 3 = black layer, 4 = white ground, 5 = transparent brownish layer, and earthen rendering. B) Chemical mappings obtained by SR-µFTIR, showing the distribution of three particular ingredients: in red, proteins; in green, carboxylates; in blue, hydrocerussite. Map size: 190 × 170 μm^2; step size: 10 × 10 μm^2. C) Average FTIR spectra obtained in the green layer (#2), the white ground layer (#4) and the transparent brownish layer (#5). The gray rectangles highlight the vibrational bands used to generate chemical mappings displayed in B).

Various components, being inorganic, organic or hybrid materials, can thus be identified and located across a complex stratigraphy with a rather good lateral resolution (10 µm here). This example is typical of sample complexity and heterogeneity in paintings, and more generally in artistic items. It demonstrates the asset of SR-FTIR for such analyses.

When one focuses on the identification of organic components, sample preparation is particularly difficult, because the use of an organic embedding medium may introduce interfering vibrational bands. Several strategies can be followed and are described elsewhere [39].

5. Current trends and outlook

As demonstrated by the constant growth of the demand for specific beamtime, the great potentiality of this technique in Archaeology and CH Science is well recognized.

For scientists that are not familiar with the operation of these centers, access to these facilities may seem restrictive. However, almost all synchrotron IR beamlines worldwide offer beam time free of charge based on a peer-reviewed proposal system. In many cases, researchers have active programs using a conventional IR microscope, equipped either with a single detector or an array detector. The synchrotron source provides a complementary capability for high spectral quality at higher spatial resolution. Since chemical changes can be very subtle, statistical analyses of spectra or images greatly benefit from high spectral quality.

One of the pitfalls of FTIR microscopy remains the diffraction limited spot size and slow data collection rates. Nowadays, focal plane array detectors are being implemented in microscopes that use a globar source, and the performance of these detectors has not yet been exploited with a synchrotron source. Clearly, the size of the detector array

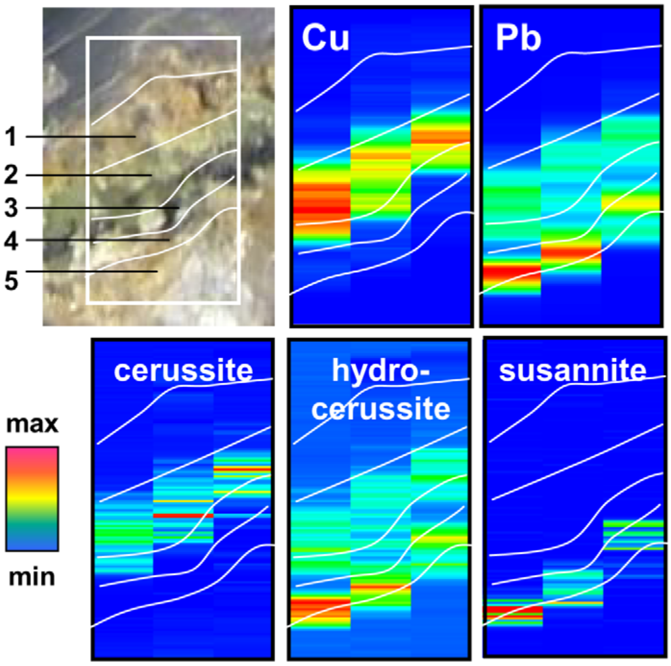

Fig. 6. Photomicrograph of sliced cross-section of sample BMM035 from Cave N(a), Bamiyan, showing a multi-layered structure: 1 = yellowish transparent layer, 2 = green layer, 3 = black layer, 4 = white ground, 5 = transparent brownish layer, and earthen rendering. Elemental and phase mappings obtained by µXRF and µXRD, respectively. Map size: 80 × 140 μm^2; beam and step size: 15 × 1 μm^2.

has to be adapted to match the projected size of the synchrotron beam, in order to keep the brightness advantage of this source. These small detector arrays might well be available soon, and will allow faster acquisition of data, and a slightly improved lateral resolution using point-spread function (PSF) deconvolution. Readers interested in the details of future improvements with such a combination of bright infrared sources with advanced bidimensional detectors can find them in [17].

Another direction for the future, which is starting to become more popular at synchrotron facilities, is the opportunity to combine IR microscopy with other synchrotron based techniques [30,31]. The strategy for efficient combination relies upon the choice of adequate sample substrates, good positioning registration between instruments, and careful coordination between beamtime allocations at different endstations. Such an IR/X-ray combination is illustrated hereafter. The example is the same painting fragment already presented in Fig. 5. In addition to FTIR microscopy, micro-X-ray fluorescence and micro X-ray diffraction were measured at the ID18F beam line (ESRF) in order to better identify inorganic phases. Details on the experimental set-up can be found in Ref. [30].

Fig. 6 shows what was achieved. The most significant elements are copper, present in the green layer, and lead, present in the green, black and white layers. Various phases were identified, corresponding to both original pigments, and alteration products. Interestingly here, a peculiar choice of lead pigments seemed to have been employed, depending on the colored layer. Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), is present in the three green, black and white layers, with a higher concentration in the white layer. Cerussite ($PbCO_3$), is specifically found in the green layer, and susannite ($Pb_4(SO_4)(CO_3)_2(OH)_2$), seems to be preferentially present in the white layer. All these lead carbonates being white, their varying relative proportions seem to indicate the use of different white lead pigments, commonly named as “lead whites”, prepared differently, or used differently.

In such a case, X-ray analyses are a very good complement to SR-FTIR: they offer helpful complementary information for band assignment; they enable identification of pigments invisible in the mid-IR region (mainly metallic oxides and sulfides); they provide a more detailed identification of phases. This multi-modal X-ray/IR approach enables going further to classical studies. It gives not only ingredients identification, but also insight on their quality and their use.

Other combinatory approaches are underway using synchrotron-based fluorescence microscopy and IR microscopy at SOLEIL synchrotron and efforts to combine scanning transmission X-ray microscopy (STXM), X-ray micro diffraction, and X-ray tomography.

Raman microscopy is also an excellent approach to vibrational spectroscopy, with an equivalent, or often better, spatial resolution than synchrotron infrared microscopy. Being more sensitive to the mineral compounds than IR, the dual use of such vibrational techniques offers a wide range of complementarities in Cultural Heritage Science. The data are complementary, but often Raman does not provide adequate spectral quality (i.e. signal to noise), data can be complicated by intrinsic fluorescence emission, and samples can suffer from laser beam damage. Thus, it is valuable to combine the two vibrational micro-spectroscopic approaches, and this should be made available for users at synchrotron facilities, such as at SOLEIL Infrared beamline.

6. Conclusion

Even if most of experiments performed on synchrotron facility exploit the X-ray domain, the interest of IR micro-spectroscopy is clearly manifested in CH Science. Its main assets are the capacity to simultaneously probe inorganic and organic materials, even in an amorphous state; and to identify and to localize them with a rather good lateral resolution. In the field of CH, these advantages are particularly beneficial in the case of hybrid materials (paintings, varnishes, cosmetics but also ancient biological samples). No doubt that synchrotron-based FTIR will find many occasions to help solving ancient craftsmen's and artist's secrets.

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