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Cultural heritage investigations at the INFN SINBAD-IR beamline

M. ROMANI(*)
INFN-Laboratori Nazionali di Frascati - Via E. Fermi 54, 00044 Frascati (RM), Italy

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Summary. — The SINBAD-IR beamline (Synchrotron Infrared Beamline At DAΦNE) situated at the INFN-Frascati National Laboratories (LNF), uses the synchrotron radiation coming from one of the bending magnets of the DAΦNE collider, for spectroscopy and imaging experiments targeting material characterization within the Infrared spectral range (FT-IR spectroscopy from THz to NIR). This study explores the increasing application of synchrotron-based techniques in the field of Cultural Heritage, specifically to characterize materials such as paintings, textiles, and archaeological tissues. The used technique are important in supporting restorers throughout diverse phases of the restoration process, including preliminary material characterization and evaluating the efficacy of the restoration treatments. The present work showcases selected applications performed at the SINBAD-IR beamline on pictorial and archaeological materials, emphasizing the inherent advantages of the methodology and discussing potential future developments.

1. – Introduction

In the field of Cultural Heritage (CH), Fourier Transform InfraRed (FT-IR) spectroscopy is routinely employed to study and characterize constituent materials and degradation products of a large variety of materials, such as paintings, textiles, archaeological remains, pottery, and many others [1-3]. The high precision and accuracy of the technique, combined with its non-destructive nature and the possibility of working on minimal quantities of sample makes it the ideal technique for the chemical and mineralogical characterization of the materials constituting the artworks [4-6]. Recently, FT-IR spectroscopy has also been increasingly used in the different phases of restoration, as example in the preliminary phases it produces information about the composition of the investigated artwork, useful to support restorers in the choice of the best operational

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(*) E-mail: `martina.romani@lnf.infn.it` methodology, while in the conclusive phases, it is used to monitor the effectiveness of the treatments (cleaning, protective materials, etc.) [7].

Considering the heterogeneity of cultural heritage materials, the possibility of using light sources with high brightness (*e.g.*, synchrotron radiation) allows to perform studies on crystalline phases and trace elements with a lateral spatial resolution not accessible by using conventional sources (5–10 μm) [1,6,8]. Indeed, by combining an IR microscope with the high brilliance of SR sources, the microscope apertures can be reduced to the diffraction limit, *i.e.*, down to a few microns in the mid-IR region [9]. At the SINBAD-IR beamline (Synchrotron Infrared Beamline At DAΦNE) of INFN-LNF DAΦNE-Light laboratory it is possible to use the synchrotron radiation emitted by one of the bending magnets of the DAΦNE collider, for spectroscopy and imaging experiments aimed to the characterization of materials in the infrared spectral range in different research fields, including material science, biology/radiobiology, cell imaging, and cultural heritage [10-12].

The radiation spectrum extends from Terahertz (THz) to Near Infrared (NIR) covering a large range infrared region (2–10000 cm^{-1}). Depending on the shape and size of the sample it is possible to work in different acquisition modes (reflection, transmission, and attenuated total reflection (ATR)) by using an optical bench (macro FT-IR) or by using an infrared microscope (micro FT-IR) [10-12]. The experimental station is adapted for each FT-IR experiment, by combining different components, such as detector, source, beam splitter, and optical windows to obtain the best experimental configuration. Indeed, the choice of the detector is strictly dependent on several factors: the characteristics of the analyzed sample (shape, size, etc.), the spectral range of the analyses, the spectral resolution, and the optical throughput (percentage of the beam reaching the detector) [12].

In the field of cultural heritage, the micro FT-IR in reflection mode is probably the most used configuration, because it allows to study microscopic samples and perform imaging analyses [6,13,14]. Indeed, by coupling an imaging detector (*i.e.*, Focal Plane Array - FPA) to an IR microscope it is possible to obtain high-resolution 2D images of the studied materials and characterize the IR signals from a spectral and spatial point of view [14,15]. This aspect is very useful for the study of the paintings' cross-sections, to characterize the materials that construct the different pictorial layers and obtain useful information about the execution techniques [14,15]. However, it should be noted that the results obtained by using micro FT-IR analysis are often affected by possible spectral distortions due to the roughness of the surface [16]. In this sense, the possibility to perform micro and macro-ATR analyses, by using dedicated microscope's objectives, allows us to obtain spectra less affected by the roughness of the surface to produce both qualitative and quantitative information [17,18]. Finally, if it is possible to perform micro-sampling, the ATR approach is commonly used to allow a preliminary fast identification and quantification of the analyzed samples, obtaining information about the inorganic and organic components, with minimal sample preparation.

However, due to the large multitude of materials constituting the cultural heritage samples, FT-IR results should ever be integrated with complementary techniques, such as X-ray fluorescence (XRF) spectroscopy, Raman spectroscopy and UV-VIS analysis to obtain a complete and exhaustive characterization of the investigated artworks. For this reason, recent technological innovations are focused on the development of multi-sensor instruments that work on an extended spectral range [19,20] coupled with data fusion approaches to obtain multi-level information of the analyzed sample [19,20].

In this work an overview of the studies carried out at the SINBAD-IR beamline on cultural heritage materials and a discussion on future developments is presented.

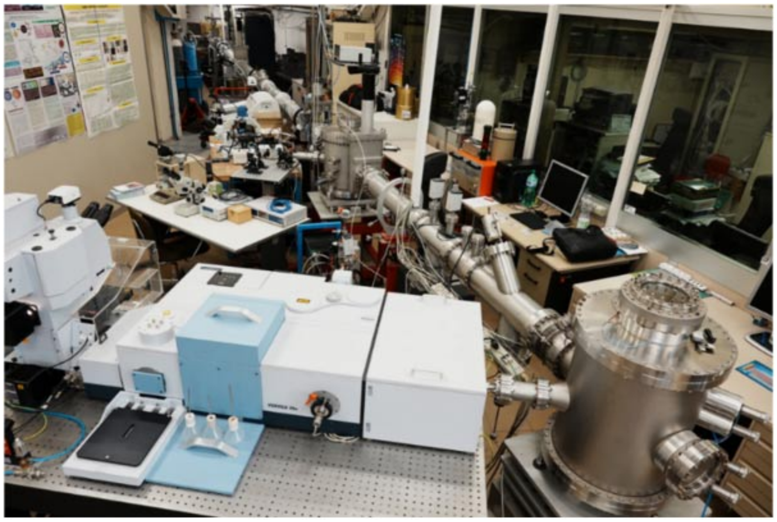

Fig. 1. – SINBAD-IR beamline at INFN-LNF DAFNE-Light laboratory.

2. – SINBAD-IR beamline characteristic and instrumentation

The SINBAD-IR beamline (see fig. 1) collects the infrared radiation, emitted by a bending magnet of the electron ring, under a 35 mrad (H) × 45 mrad (V) solid angle and afterwards transmitted by an optical system consisting of six Au-coated mirrors to two end stations at a distance of about 25 m [10, 11].

The experimental end station is composed by a Vertex70v interferometer equipped with three detectors a DTGS (10–10000 cm^{-1}), a MCT (5000–600 cm^{-1}) and a bolometer (2–300 cm^{-1}). The interferometer is coupled with a Hyperion 3000 IR microscope (Bruker Optik, Germany) equipped with a 64 × 64 pixels Focal Plane Array imaging detector to perform chemical imaging of the analyzed samples in the spectral range, 850–5500 cm^{-1}, and a single point MCT detector (10000–600 cm^{-1}). The beamline instrumentation also includes a diffuse reflectance unit (DRIFT), a diamond Attenuated Total Reflection (ATR) module and a micro-ATR objective (20×). The laboratory is also equipped with a second FT-IR spectrometer, Tensor II, mainly dedicated to ATR and HTS-XT measurements, a stand-alone IR microscope LUMOS II, and a portable FT-IR spectrometer R-Alpha II. All reported FT-IR devices are from Bruker Optik, Germany. To perform complementary analyses other laboratory facilities are available for the study and preparation of the analyzed samples.

3. – Results and discussion

3˙1. *Archeological textile artefacts.* – FT-IR spectroscopy is commonly used to characterize modern and archaeological fibers allowing an easy identification between animal and plant fibers, due to the presence of characteristic absorption bands, as amide (1690, 1540, 1260 cm^{-1}) and cellulose (5000–4600 cm^{-1} (($\nu + \delta$)OH, δOH, 2 νCO); 4400–4300 cm^{-1} (($\nu + \delta$)CH, 2δCH); 4262 cm^{-1} (-CHx combination stretching); 4330 cm^{-1} (-CHx combination stretching); 4720 cm^{-1} (C-O stretching, OH); 1595 cm^{-1} (C=C); 1505 cm^{-1}; 1155 cm^{-1} (aromatic ring C-C); 1105 cm^{-1} (C-O-C) [5, 19, 20].

Regarding the characterization of vegetable fibers by using ATR spectroscopy we noticed that the discrimination between modern plant fibers is possible thanks to the presence of characteristic spectral features. Otherwise, when the fibers to be analyzed come from archaeological context their identification result to be more complicated or even impossible. This happens because the conservation conditions in the archaeological context it can produce oxidation effect that could alter the IR spectra of the samples, especially in specific spectral region such as the lipidic (3000–2700 cm^{-1}) and the carbonyl (1750–780 cm^{-1}) ones, making them indistinguishable from each other. The use of SR radiation for this type of application could be useful to improve the S/N ratio, especially in the CH-region often affected by noise. However, in the case of unknown archaeological fibers it could be useful to complement FT-IR results whit other analyses such as Raman spectroscopy or morphological analysis. Finally, the possibility to have a spectral database containing IR spectra of modern fibers and IR spectra of the same fibers artificially aged could help the spectroscopist in the identification of unknown samples [5, 19, 20].

3˙2. *Archeological human remains bones, hairs and teeth.* – The study of archaeological human remains by IR spectroscopy allows to obtain information about their mineralogical and organic composition such as the presence of the phosphate's groups at 450 cm^{-1} (ν2PO4-3) and 590–584 cm^{-1} (ν4PO4-3), the apatite bands at 960 cm^{-1} (ν1PO4-3), and the bands related to the presence of organic components (1650 cm^{-1} (amide I), 1500–1550 cm^{-1} (amide II) and 1200–1300 cm^{-1}) [21-23]. At SINBAD-IR in recent years we have analyzed different archaeological humans remains and for example, in the case of archaeological bones we usually perform ATR analyses to obtain a preliminary fast identification and quantification of the entire bone matrix. The ATR spectra were also used to calculate the ratios between the absorption IR bands of constituents involved in diagenetic process giving information about their conservation (state of mineralization, presence of organic matter, etc.) [21-23]. Using the ATR accessory, it is possible to heat the sample up to a temperature of 150 °C to monitoring the dynamics of the bone's compounds and to evaluate how the temperature affects the IR spectra (*e.g.*, degradation of organic components like collagen) to obtain information about the thermal effects that could occur to archaeological bones during the years [24]. By using SR radiation, it is possible to analyze areas of size between 5–10 μm through the acquisition of single point spectra with a high lateral spatial resolution and a high S/N ratio. This Information on preservation status of archaeological bones giving to archaeologist's precious information about the life habit of ancient population, and this information can be useful to plan other analysis, such as isotopic or radiocarbon dating analyses [21-23].

3˙3. *Paintings materials.* – FT-IR spectroscopy in reflection mode is extensively used for the identification of cross-section painting materials, giving information on the stratification of the painting. This technique is also used for the characterization of residues of degradation products on painted surfaces, which not only compromise the aesthetic effect but also represent a potential risk for their conservation [25, 26]. In particular, FT-IR spectroscopy allows the identification of metal oxalates and carboxylates, which represent the most widespread degradation products in both ancient and modern paintings. Figure 2 shows the results obtained on a stratigraphic cross-section from a fresco completely covered by a yellowing patina, in this case micro-FT-IR analyses were carried out to identify the materials constituting the patina.

The obtained results showed that the patina is constituted of silicates (absorption centered at 1130 cm^{-1} and 1030 cm^{-1}) and calcium carbonate (1450 cm^{-1}). Therefore,

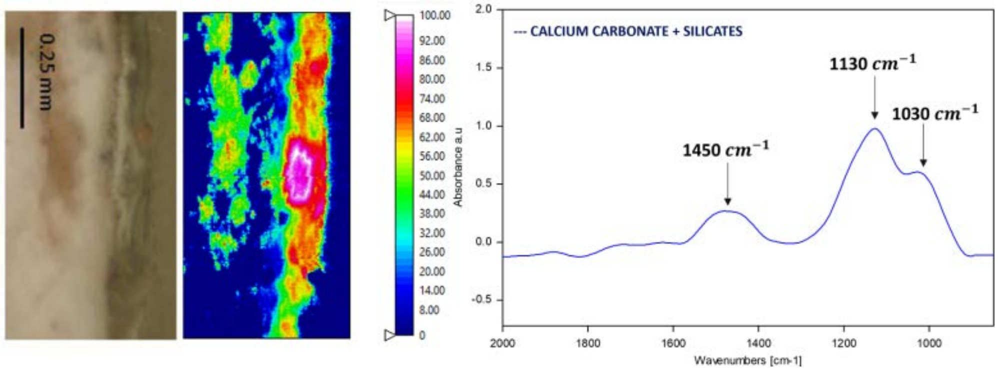

Fig. 2. – FT-IR analyses performed on a stratigraphic cross-section of a fresco completely covered by a yellowing patina. The obtained results showed that the patina is constituted of silicates, calcium carbonate, nitrates.

based on the results obtained, it is presumable that the silicates contained in the wall structure were transported to the surface through water infiltrations. This long-term effect can lead to the formation of white scales of silicon dioxide (opal), or silicate mixed with other substances, in particular calcium carbonate. The identification of degradation products and patinas on painted surfaces is a key issue to define the best strategies for restoration treatments.

3˙4. *Future developments*. – In the field of Cultural Heritage, the possibility of carrying out *in situ* analyses has become mandatory both when the work to be analyzed is immovable and when it is not possible to carry out micro sampling needed to support restorers during the different phases of the restoration. For this reason, in the last year, DAΦNE-Light laboratory has been equipped with a portable IR spectrometer to perform FT-IR analyses directly *in situ*. Moreover, considering the assumption that the analysis of the chemical composition of paintings can be more exhaustive using a multi spectral approach since each spectral range can give complementary information, a scanning system, MT-FTIR scanner, able to acquire spectroscopic images using different techniques (XRF, UV-VIS fluorescence and reflection FT-IR) operating in a broad extended spectral range (from X-rays to MIR) acquiring both the elemental and molecular composition on the same area with high precision, has been developed. The acquired data can be recombined giving rise to hyper-spectral images of the painting containing all the different information. Nowadays the multi-techniques, MT-FTIR scanner, has been successfully tested on several modern and contemporary paintings giving information about their composition and their conservation state [27].

4. – Conclusions

In this work some applications to study cultural heritage materials using FT-IR spectroscopy at the SINBAD-IR beamline of INFN-LNF DAΦNE-Light laboratory have been presented. The techniques here described are confirmed to be valid tools to study and characterize pictorial and archaeological materials coupling to the possibility to use synchrotron radiation to perform studies on crystalline phases and trace elements with a lateral spatial resolution not accessible by using conventional sources (5–10 micron). Finally, a new MT-multi techniques scanner for *in situ* analysis was developed with the aim to obtain a complete characterization of the studied artworks by integrating several complementary techniques in the same instrument.

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