Diagnostic techniques for cultural heritage: applications of Synchrotron Fourier Transform Infrared (FT-IR) spectroscopy

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Sinbad IR beamline @ DaΦne

INFN-International Masterclass 2017
The scientific approach to conservation
Principles of FT-IR spectroscopy
Sampling techniques: transmission, reflection, Attenuated total reflection (ATR) and Diffuse reflection (DRIFT)
Infrared imaging and microscopy: chemical images
FT-IR Analysis of a painting cross section
The scientific approach to conservation

- Material ageing, climate change, atmospheric pollution, anthropic pressure...
- Inappropriate conservation and restoration procedures have also contributed to degradation of artworks
- The modern approach to conservation requires a deep scientific investigation before any treatment
In situ diagnostic

Laboratory diagnostic

Conservation

Monitoring
Sampling techniques

- Non destructive
- Micro destructive
Reflectance
IR Reflectance
UV fluorescence
X ray radiography
FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR): physical principles
The electromagnetic spectrum describes the various types of electromagnetic energy based on wavelength.
William Herschel (1738-1822)
Visible and IR light are both EM radiation, differing only for the wavelength. They both propagate in vacuum at the light speed $c$.

- Wavelength $\lambda$ (μm)
- Frequency $\nu$ (Hz: $\nu=c/\lambda$)
- Energy $E$ (eV: $E=\hbar\nu$)
- Wavenumber $\tilde{\nu}$ (cm$^{-1}$)

$$\tilde{\nu} \text{ (cm}^{-1}) = \frac{1}{\lambda} \text{ (cm)}$$
What happens when «light» interacts with matter

<table>
<thead>
<tr>
<th>Change of spin</th>
<th>Change of orientation</th>
<th>Change of configuration</th>
<th>Change of electron distribution</th>
<th>Change of nuclear configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.m.r.</td>
<td>E.s.r.</td>
<td>Microwave</td>
<td>Infra-red</td>
<td>Visible and ultra-violet</td>
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<tr>
<td><img src="image1" alt="N.m.r. diagram" /></td>
<td><img src="image2" alt="E.s.r. diagram" /></td>
<td><img src="image3" alt="Microwave diagram" /></td>
<td><img src="image4" alt="Infra-red diagram" /></td>
<td><img src="image5" alt="Visible and ultra-violet diagram" /></td>
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<thead>
<tr>
<th></th>
<th></th>
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<th>10 cm⁻¹</th>
<th>10⁶ Wavenumber</th>
<th>10⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 m</td>
<td>100 cm</td>
<td>1 cm</td>
<td>100 μm</td>
<td>1 μm</td>
<td>10 nm Wavelength</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>3 x 10⁶</th>
<th>3 x 10⁸</th>
<th>3 x 10¹⁰</th>
<th>3 x 10¹²</th>
<th>3 x 10¹⁴</th>
<th>Hz</th>
<th>3 x 10¹⁶ Frequency</th>
<th>3 x 10¹⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻³</td>
<td>10⁻¹</td>
<td>10</td>
<td>10³</td>
<td>10⁵ joules/mole</td>
<td>10⁷ Energy</td>
<td>10⁹</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
In the simple case of two point charges, one with charge $+q$ and the other one with charge $-q$, the electric dipole moment $p$ is:

$$p = qd$$

$d$ is the displacement vector pointing from the negative charge to the positive charge. Thus, the electric dipole moment vector $p$ points from the negative charge to the positive charge.
Polar molecules

When one end of the molecule is slightly positive and one end is slightly negative
Common examples of non-polar gases are the noble or inert gases, including:
* Helium (He)
* Neon (Ne)
* Krypton (Kr)
* Xenon (Xe)

Other non-polar gases include:
* Hydrogen (H₂)
* Nitrogen (N₂)
* Oxygen (O₂)
IR active modes

* $O_2$, $H_2$, $Cl_2$, $N_2$ are not IR active!
Increasing $k$ (bond strength) the frequency increases
Decreasing $m$, the frequency increases.
Normal modes of vibration

\[ E = \left(n + \frac{1}{2}\right) \hbar \]

(quantized energy levels)

* 3N-6 (non linear molecule)
* 3N -5 (linear molecule)
Single bonds: C-C, C-O, C-N $\rightarrow$ 800 - 1300 cm$^{-1}$
Double bonds: C=C, C=O, C=N $\rightarrow$ 1700-1900 cm$^{-1}$
Triple bonds: C≡C, C≡N $\rightarrow$ 2000-2300 cm$^{-1}$

C-H, N-H, O-H $\rightarrow$ 2700-3800 cm$^{-1}$
Every molecule has its unique IR spectrum
So, what Information can FT-IR Provide?

• It can identify unknown materials

• It can determine the quality or consistency of a sample

• It can determine the amount of components in a mixture
Also very complex molecules...
Fourier Transform Infrared Spectroscopy (FT-IR)
IR sources
Synchrotron radiation
The electromagnetic radiation emitted when charged particles are accelerated radially \((a \perp v)\) is called **synchrotron radiation**.

Classic \((v \ll c)\)

\[(c = \text{speed of light})\]

Relativistic \((v \approx c)\)

\[
\beta = \frac{v}{c} \\
\gamma = \frac{1}{\sqrt{1 - \beta^2}}
\]

Per \(\beta = 0.99\) \(1/\gamma = 10\) mrad

**Brilliance**

\[
\text{brilliance} = \frac{\text{photons}}{\text{second} \cdot \text{mrad}^2 \cdot \text{mm}^2 \cdot 0.1\%BW}
\]
strongly bundled
polarized
precisely calculable
temporal structure
high intensity
large energy range
The beamlines

- Magnet
- Synchrotron Light

- Brilliance
- Photon Energy [keV]
- Undulator
- Wiggler
- Bending magnet

Diagram showing the layout and components of the beamlines.
The IR SINBAD beamline

Infrared domain
from 10 to $10^3$ cm$^{-1}$
1.24 meV to 1.24 eV
Michelson interferometer
The interferogram depends on the **optical path difference (OPD)** between the two beams.

The OPD is twice the mirror excursion $x$. Since the mirror speed $v$ is constant:

$$2x = 2vt$$
OPD = 2n \frac{\lambda}{2} \quad (n = 0, \pm 1, \pm 2, \ldots)

OPD = (2n+1) \frac{\lambda}{2} \quad (n = 0, \pm 1, \pm 2, \ldots)
Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make an identification, the measured interferogram signal can not be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the **Fourier transformation**. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.
Origin of the interferogram: the monochromatic wave
Origin of the interferogram: the polychromatic wave (discrete frequencies)
Origin of the interferogram: the policromatic wave (continuous frequencies)
$$S(v) = \int_{-\infty}^{\infty} I(x)e^{i2\pi vx} \, dx$$
Measuring an IR spectrum: two ways to look at FTIR data

TRANSMITTANCE

\[ T = \frac{I\text{ (sample)}}{I\text{(reference)}} \]
ABSORBANCE

\[ A = -\log T \]
Beer-Lambert law

Absorbance is proportional to the concentration

\[ A = \log \frac{I_0}{I} = \varepsilon \cdot C \cdot b \]

\( \varepsilon = \) absorption coefficient
\( C = \) concentration
\( b = \) sample thickness
Sampling techniques
Depending on the sample form (solid, liquid, powder, film) and which characteristics you want to maintain, it is possible to use different sampling techniques, **destructive** or **non-destructive**: 

- Transmission (liquids, powders, thin sections)
- Specular reflection (crystals, polished sections)
- Diffuse reflectance (powders)
- Attenuated Total Reflection (ATR) (thick samples, non-reflecting surfaces)
Transmission
KBr powder pellets

- Invasive 😞
- Destructive 😞
- Time consuming 😞
- Very precise (absolute measurement) 😊
- Spectral database 😊
Background \((I_0)\)

Sample \((I)\)

\[
T = \frac{I}{I_0} \quad A = \log \frac{1}{T} = -\log T
\]
Reflection spectroscopy

Preparation of the surface – polishing 😞
Thick samples 😊
Attenuated Total Reflection (ATR)
Principles of Attenuated Total Reflection spectroscopy (ATR)

Snell’s law: 
\[ n_1 \times \sin \Theta_i = n_2 \times \sin \Theta_r \]

Critical angle: 
\[ \Theta_r = 90^\circ \]
\[ \sin \Theta_c = \frac{n_2}{n_1} \]

(es. 38° for ZnSe for a sample with n=1.5)
Penetration depth

\[ dp = \frac{\lambda}{2 \pi n_1 \left( \sin^2 \theta_i - n_{21}^2 \right)^{1/2}} \]

<table>
<thead>
<tr>
<th>( \theta_i )</th>
<th>30°</th>
<th>45°</th>
<th>60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRS-5</td>
<td>( i \lambda )</td>
<td>0.290( \lambda )</td>
<td>0.113( \lambda )</td>
</tr>
<tr>
<td>Ge</td>
<td>0.091( \lambda )</td>
<td>0.041( \lambda )</td>
<td>0.002( \lambda )</td>
</tr>
</tbody>
</table>

\( i = \text{total transmission, sample index} = 1.5 \)
$$d_P \propto \lambda$$

$$\text{ATR} = \frac{AB \times \nu [\text{cm}^{-1}]}{1000 [\text{cm}^{-1}]}$$
Quick

Non invasive

(semi)destructive

Fig. 2. Detail of a cross-section from the polychrome sculpture (Fig.2): (a) visible microscopic image; (b) image of sample under ultraviolet light; (c) FT-IR image created by plotting the integrated absorbance of the embedding resin band between 1330 and 1200 cm\(^{-1}\); (d) FT-IR image showing the distribution of the silicate integrated absorbance between 1050 and 1000 cm\(^{-1}\); (e) FT-IR image showing the distribution of the azurite integrated absorbance between 970 and 920 cm\(^{-1}\); (f) FT-IR image showing the distribution of the carbonate integrated absorbance between 1335 and 1440 cm\(^{-1}\); (g) FT-IR image showing the distribution of the amide II integrated absorbance between 1580 and 1480 cm\(^{-1}\); (h) FT-IR image showing the distribution of the triglycerides integrated absorbance between 1765 and 1725 cm\(^{-1}\); (i) FT-IR spectrum extracted from the right area of h, marked sp1. The size of the FT-IR images is 700 \(\mu\)m \(\times\) 500 \(\mu\)m. The figure is available in colour in the online version via Science Direct.
ATR spectrum of gypsum

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]
\[
\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}
\]
\[
\text{CaSO}_4
\]

Water molecule:
- Stretching symmetric and antisymmetric of \( \text{H}_2\text{O} \)
- \( v_3 \) Stretching antisymmetric of \( \text{SO}_4 \) tetrahedra
- \( v_1 \) Stretching symmetric of \( \text{SO}_4 \) tetrahedra
CaSO₄·2H₂O

CaCO₃
What if the sample is VERY small?
Microscopy and Imaging
The microscope is essentially a beam condenser.

The IR microscope is essentially a beam condenser.

\[ NA = n \cdot \sin 2\theta \]
FTIR imaging

Study of the patina sample from a Dogon statuette:

a) Photograph of the object, Quai Branly Museum, inventory no 71.1935.105.109, (copyright C2RMF, D. Vigeaars);
b) Dark field microscopic view of the cross-section of the sample;
c) Backscattered electron micrograph;
d) ToF-SIMS image of protein fragment ions;
e) SR-μFTIR image of proteins.

Analytical Chemistry. DOI: 10.1021/ac070993k
Mapping vs imaging

Mapping:

- Campione
- Stage portacampioni automatico gestito da PC
- Rivelatore a singolo elemento (MCT, 250μm)

Total acquisition time:
TAT = N x M x t

Ex
- t = 30 sec
- N = M = 20
- TAT = 600 sec
Figura 2: (a) Lo spettro IR di un composto organico mostra gli assorbimenti dovuti alle vibrazioni molecolari. (b) Schema ottico del microscopio IR accoppiato allo spettrometro ed al detector FPA. (c) Schema di funzionamento di un detector FPA.
Imaging:

- Campione
- Stage portacampioni non necessariamente automatico
- Focal Plane Array Detector (64x64, 128x128, 256x256 – pixel da 40\(\mu\)m)

Total acquisition time: 
TAT=t

In t we are acquiring a NxN matrix of spectra
APPLICATION TO THE STUDY OF PAINTING CROSS SECTIONS
Figura 1. Sezione stratigrafica di un frammento prelevato dalla veste verde di un dipinto raffigurante la Madonna col Bambino: a) sezione stratigrafia al microscopio ottico in luce visibile; b) immagine ottenuta al microscopio elettronico (SEM); c) mappatura dell’elemento rame (Cu) eseguita mediante spettrometro a raggi X al microscopio elettronico (SEM-EDS); d) distribuzione della resina poliestere ottenuta mediante FTIR FPA-imaging; e) distribuzione del pigmento verde malachite, ottenuta mediante FTIR FPA-imaging; f) distribuzione di legante proteico, ottenuta mediante FTIR FPA-imaging; g) distribuzione di olio siccativo ottenuta mediante FTIR FPA-imaging; h) spettro di assorbimento della particella verde e del riferimento della malachite; i) spettro della componente proteica e del riferimento del rosso d’uovo; j) spettro ottenuto da una zona contenente olio siccativo e lo spettro di riferimento di una “sapone” formatosi per reazione tra rame e olio siccativo – immagine tratta dal testo citato – nota 3
LED lights may be bad for Van Gogh Paintings

The darkening of chrome yellow is a phenomenon widely observed on several paintings by Vincent van Gogh such as the famous versions of the Sunflowers. Analysis of artificially aged model samples of lead chromate using the combined use of various synchrotron radiation based analytical techniques ($\mu$-XRD, $\mu$-XANES and $\mu$-FTIR), established that darkening of chrome yellow is caused by reduction of PbCrO$_4$ to Cr$_2$O$_3$.2H$_2$O (viridian green). This is likely accompanied by the presence of another Cr(III) compound, such as either Cr$_2$(SO$_4$)$_3$.H$_2$O or (CH$_3$CO$_2$)$_2$Cr$_3$(OH)$_2$ [chromium(III) acetate hydroxide].
Phosphor-based white LED light

To avoid photo induced darkening of the susceptible variants of the lead chromate-based pigments, it is advisable to minimize their exposure to light with wavelengths shorter than about 525 nm
Combined use of Synchrotron Radiation Based Techniques for Revealing an Alternative Degradation Pathway of the Pigment Cadmium Yellow in a Painting by Van Gogh
Fourier Transform Infrared Spectroscopy (FT-IR) @ LNF

Sulphate [SO$_4^{2-}$] content

monoclinic $\rightarrow$ orthorombic
Septimius Severus’s Arch degradation products

200x600 μm
MICRO FT-IR chemical imaging
Multivariate analysis combined with FT-IR

Cluster Analysis

Principal Component Analysis

RGB map of the sample composition
Tuissues preservation of 16-18th century mummies

Skin

Stereo microscope (Optika SZM-2) images (4.5x) of skin (P81, left shoulder)

SEM images show collagen fibers strongly dehydrated and stiffened, arranged in bundles partially broken and unrolled, in different preservation states. High resolution images reveal the collagen periodical band pattern (A) and assembled Type I and IV collagen fibers (B).

(M.G. Bridelli et al, Università degli studi di Parma)
Bones

Stereo microscope (Optika SZM-2) image (4.5x) of compact bone, transverse section (S81, right femur)
Hair
Il carbonile

Solventi
Leganti
Vernici
Fibre

Ma anche in alcuni pigmenti inorganici
Gli esteri

- Olii siccativi
- Resine naturali
- Cere
- Resine sintetiche
- Additivi
- Plastiche
Le ammidi

Struttura generale di un'ammide. Se R' e R" sono idrogeni l'ammide si dice primaria, se solo uno fra R' ed R" è un H, si dice secondaria, se R' ed R" non sono idrogeni, l'ammide si dice terziaria

Tempere all’uovo
Tempera grassa
Lana e seta
Colle animali
Cuoio e pelle
Caseina
Plastica
I polysaccaridi

Acquerello
Gomme naturali
Legno
Carta
Fibre vegetali

Acquerello
Legno e carta

Gomma arabica
Gomma adragante
I pigmenti

- Carbonati
- Silicati
- Solfati
- Pigmenti organici
Prodotti di degrado comuni

- Solfati
- Ossalati
- Nitrati
- Saponi
DAFNE-Light

DAFNE-Light is the Synchrotron Radiation Facility at the Laboratori Nazionali di Frascati (LNF).

Three beamlines are operational using, in parasitic and dedicated mode, the intense photon emission of DAFNE, a 0.51 GeV storage ring with a routinely circulating electron current higher than 1 Ampere. Two of these beamlines (DXR1 and DXR2) have one of the DAFNE wigglers magnets as synchrotron radiation source, while the third beamline (SINBAD-IR) collects the radiation from a bending magnet. Now XUV bending magnet beamlines are nowadays under construction.

The beamlines DXR1 and SINBAD-IR are open to external users.

https://web2.infn.it/Dafne_Light/
cestelli@lnf.infn.it
ATR spectrum of gypsum

CaSO$_4$·2H$_2$O

CaSO$_4$·0.5H$_2$O

CaSO$_4$

Water molecule:
Stretching symmetric and antisymmetric of H$_2$O
$v_3$ Stretching antisymmetric of SO$_4$ tetrahedra
$v_1$ Stretching symmetric of SO$_4$ tetrahedra
CaSO$_4$·2H$_2$O

CaCO$_3$