

Applications of Raman spectroscopy to Cultural Heritage

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Collaborations

Organisations devoted to the Cultural Heritage conservation and restoration

- Istituto Centrale per la Patologia del Libro (I.C.P.L)
- Istituto Centrale del Restauro (I.C.R.)
- Soprintendenza Archeologica di Roma
- Soprintendenza Archeologica di Napoli e Caserta
- Pontificia Commissione di Archeologia Sacra

University Departments

- Dipartimento di Fisica "E. Amaldi", Università "Roma Tre"
- Dipartimento di Studi storico-artistici, archeologici sulla conservazione, Università "Roma Tre"
- Dipartimento di Mineralogia, Università di Padova

Research Organisations

- UdR I.N.F.M. di Roma Tre e de L'Aquila
- I.C.T.I.M.A. CNR (Padova)
- I.F.A.M. CNR (Pisa)
- LANDIS, Laboratori Nazionali del Sud, INFN (Catania)

Contributions of the scientific methodologies to Cultural Heritage

The main purposes of the art objects study are:

- **Historical and technological knowledge**
 - materials and execution technique analyses
 - dating and authenticating
- **Restoration**
 - degradation state study
 - individuation of the previous restoration treatments
 - choice of new products for restoration
 - control and set up of conservation treatment and conditions (micro-climate)
- **Fraud repression**

In order to be employed in Cultural Heritage field, analytical techniques must:

- be non-destructive or at most micro-destructive
- have a high spatial resolution
- have a high sensitivity

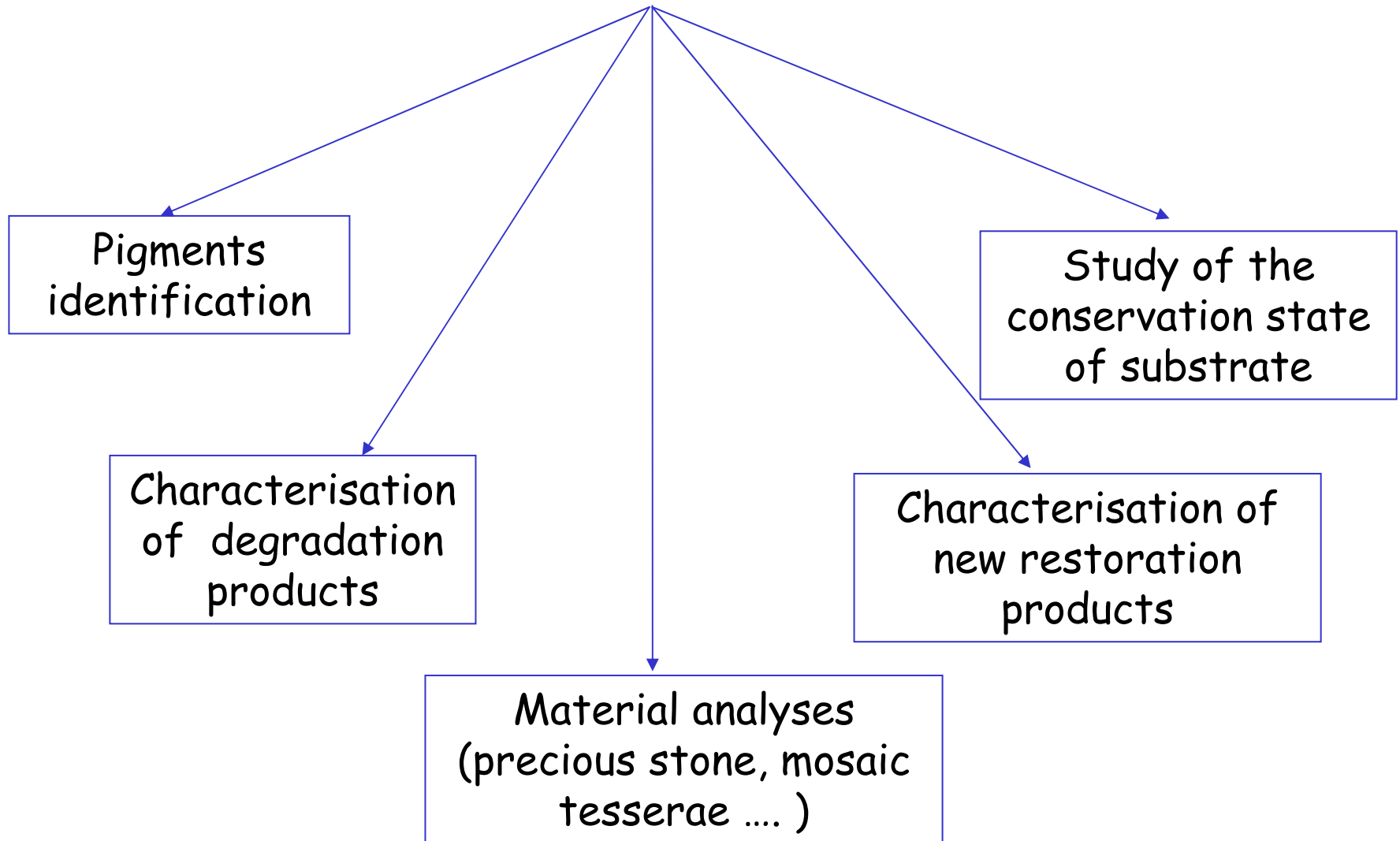
Main techniques to investigate Cultural Heritage

- **Dating techniques:**
C 14, high resolution mass spectroscopy, dendrochronology, thermo-luminescence.....
- **Tomographic techniques:**
X o γ rays, ultrasounds, IR reflectography, NMR, thermography.....
- **Spectroscopic techniques:**
X e neutron diffraction, IR-Vis.-UV absorption and reflectance, **Raman Spectroscopy**, Mossbauer, NMR, Fluorescence (XRF, α -PIXE, p-PIXE, LIBS), mass spectroscopy, **XANES**, **EXAFS**.

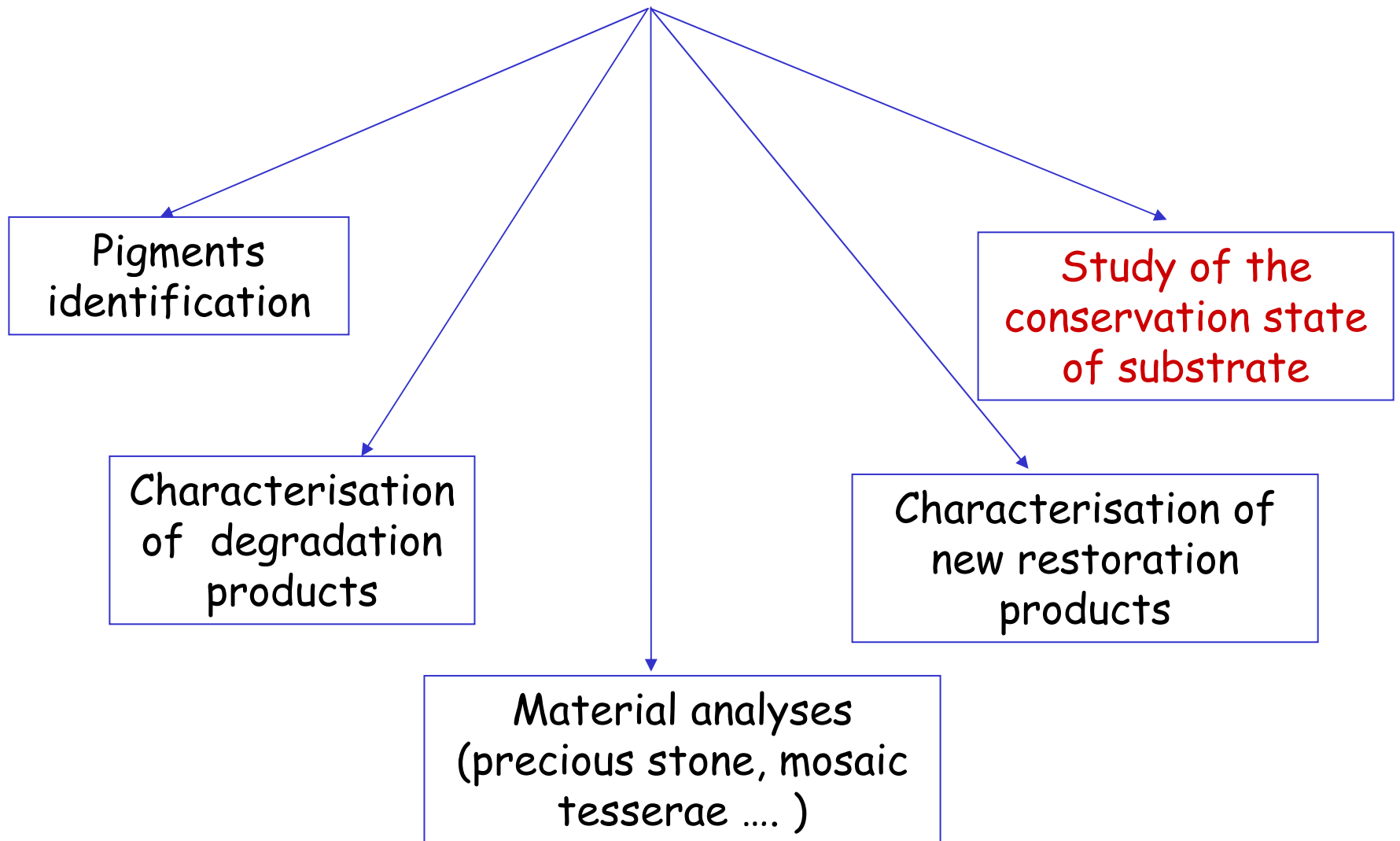
Advantages of Micro Raman Spectroscopy to Cultural Heritage field

- ◆ it is very sensitive to analyse and identify the compounds, because each scattering species gives its own characteristic vibrational Raman spectrum, which can be used for its qualitative identification.
- ◆ the measurements require only few minutes
- ◆ the technique is absolutely non-destructive; it is possible to perform measurements without sampling the masterpiece
- ◆ it has a high spatial resolution
- ◆ the technique is not particularly sensitive to the presence of bonded water

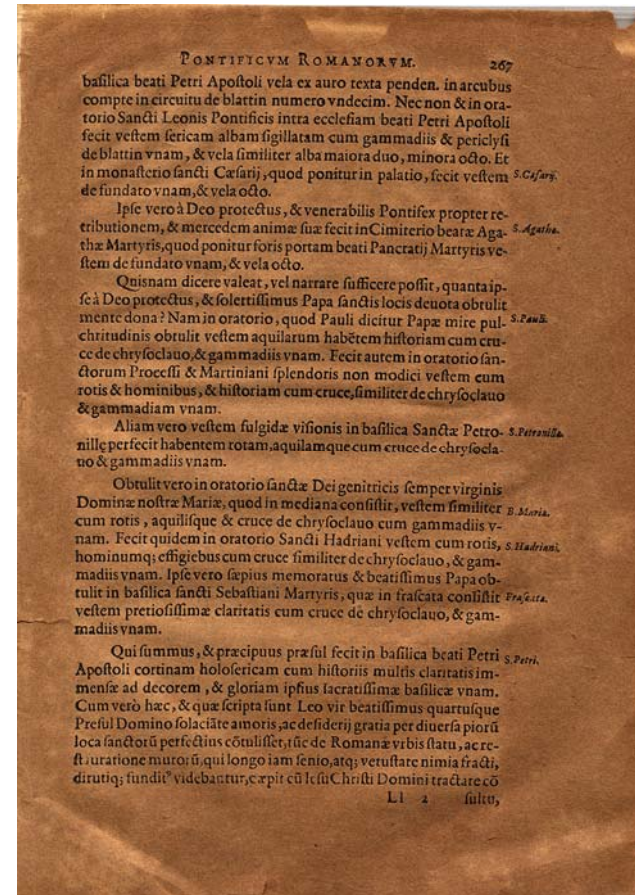
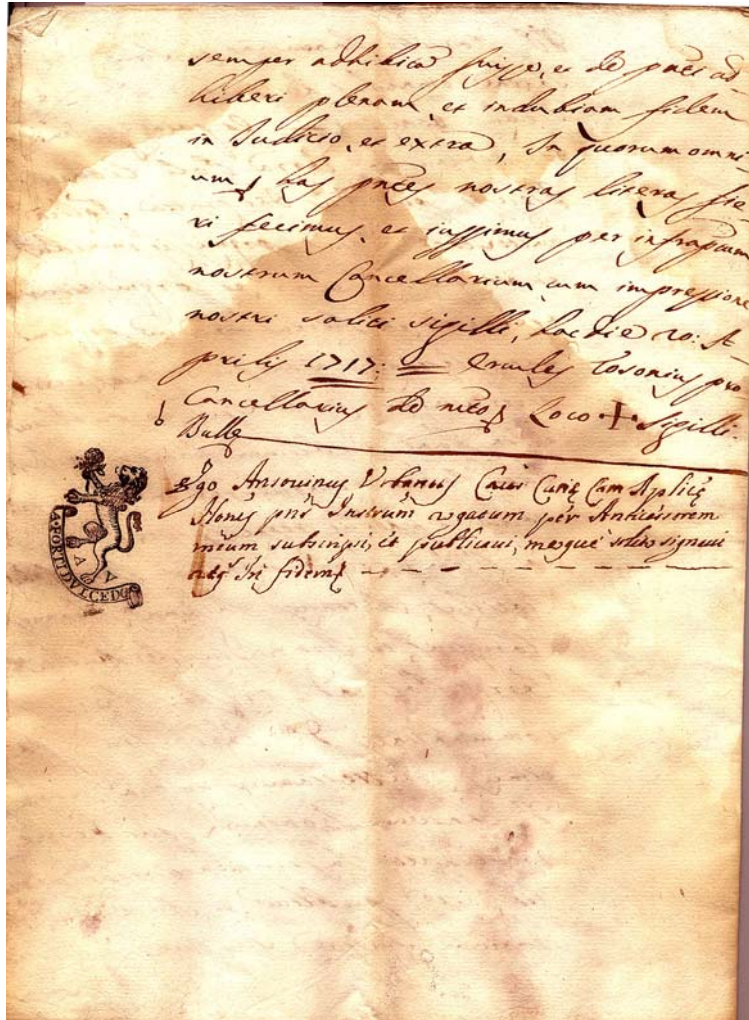
Applications of Raman Spectroscopy to Cultural Heritage



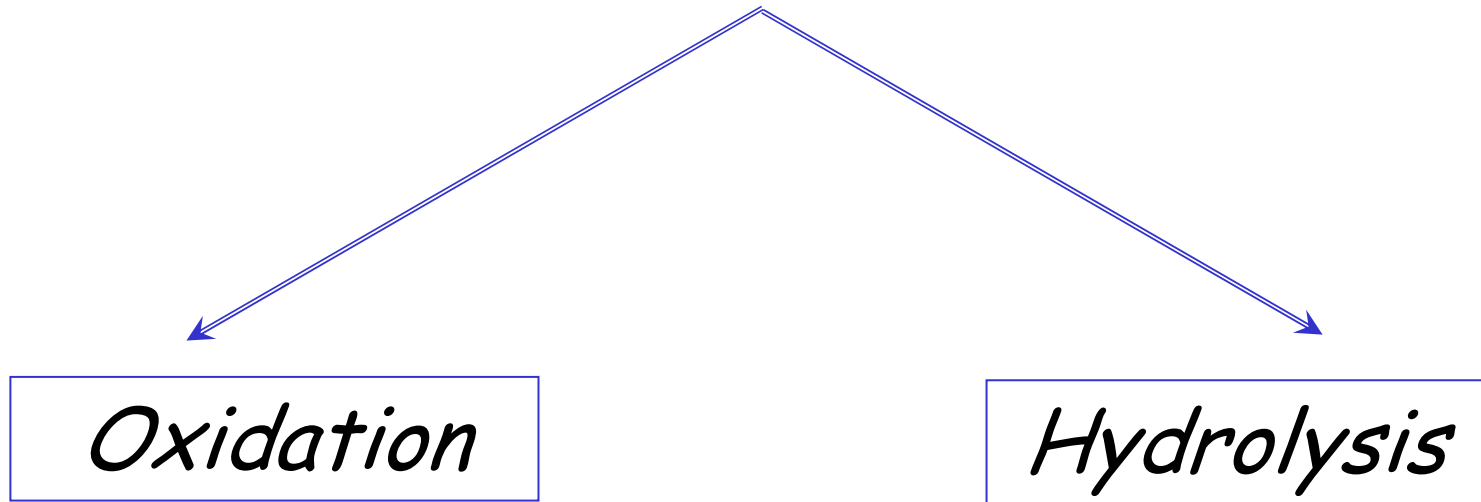
Applications of Raman Spectroscopy to Cultural Heritage



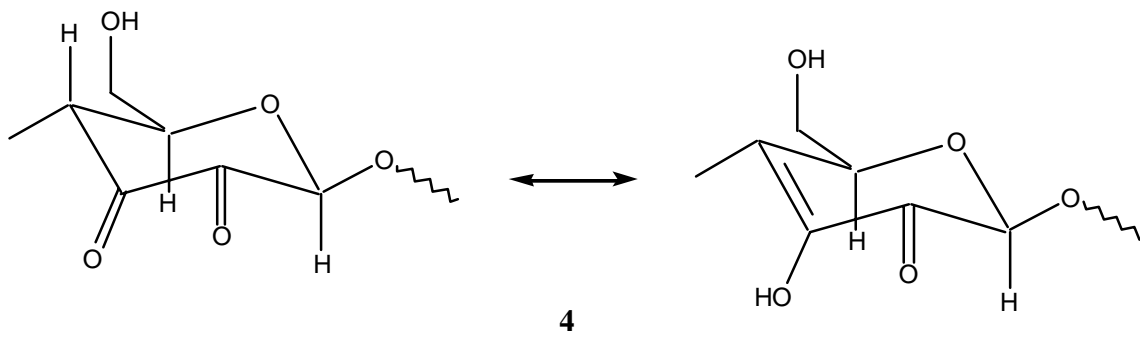
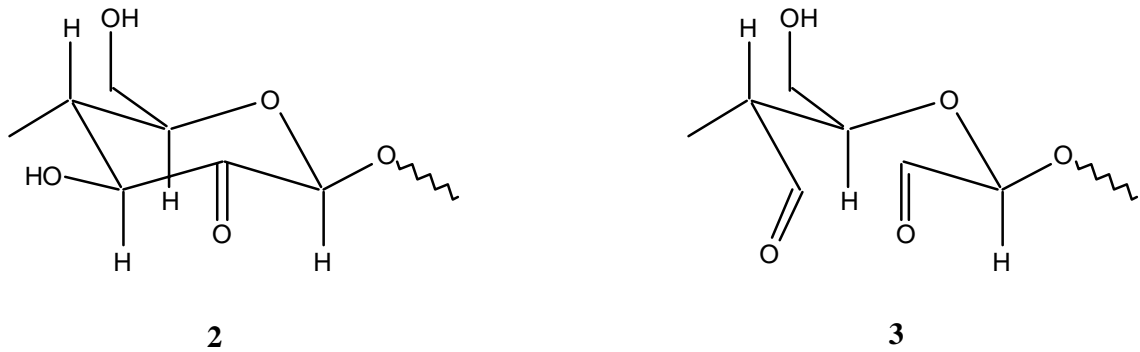
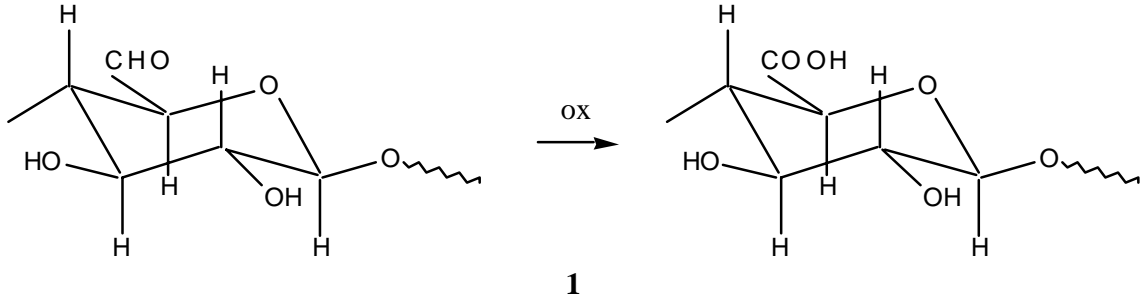
Study of the degradation processes in paper



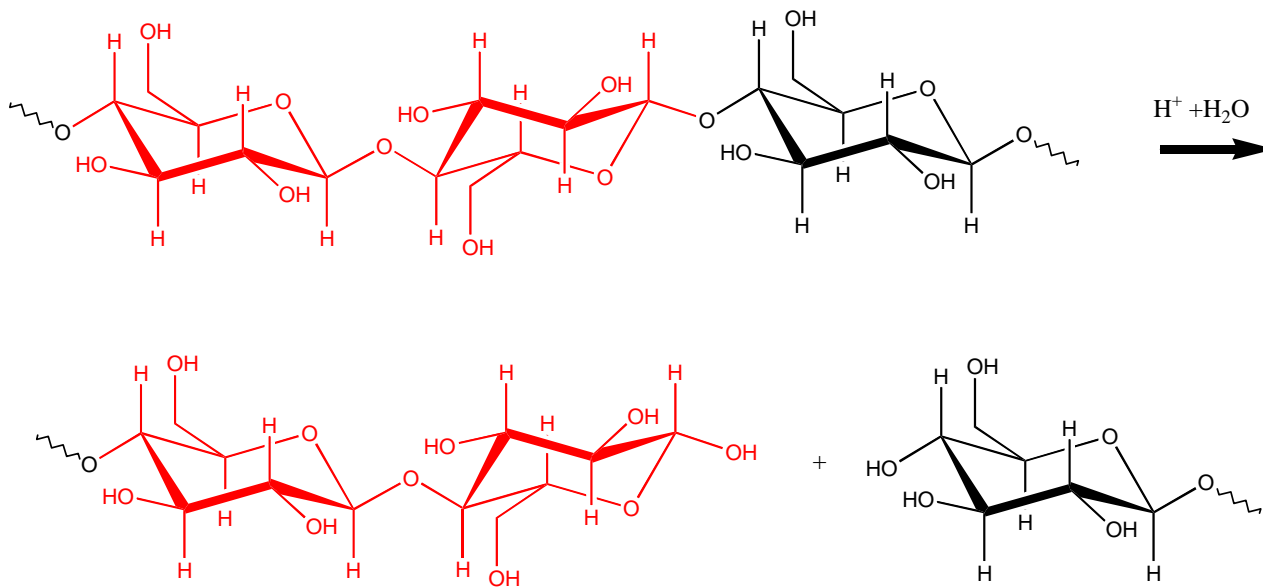
Main degradation mechanisms that can take place in paper



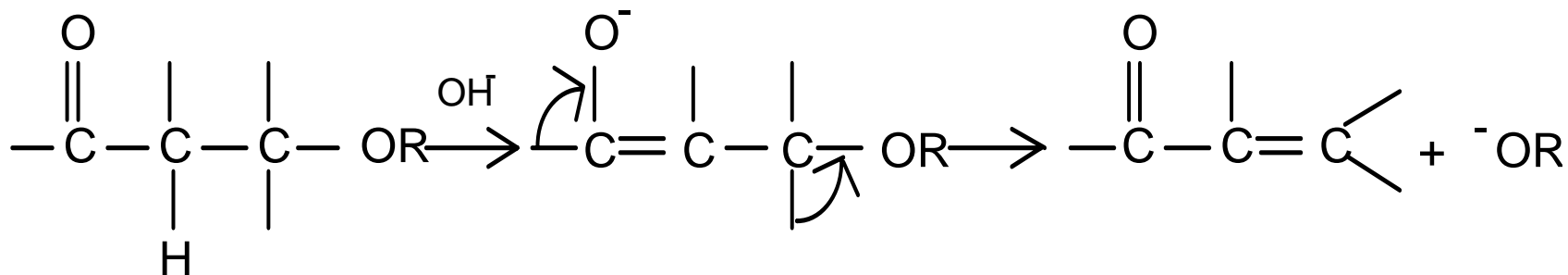
Oxidation



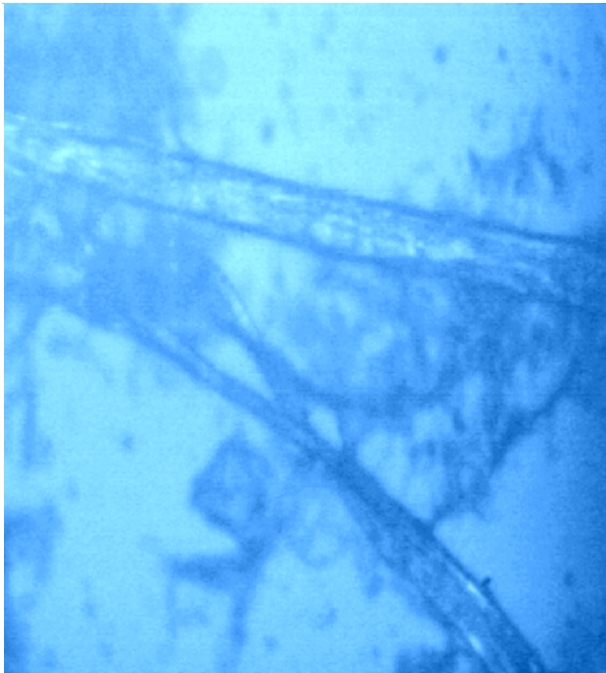
Hydrolysis



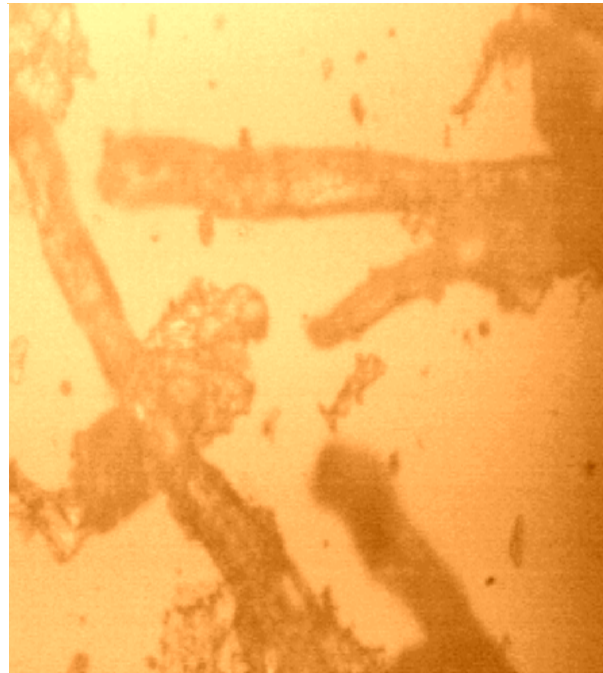
β -alcoxy elimination mechanism



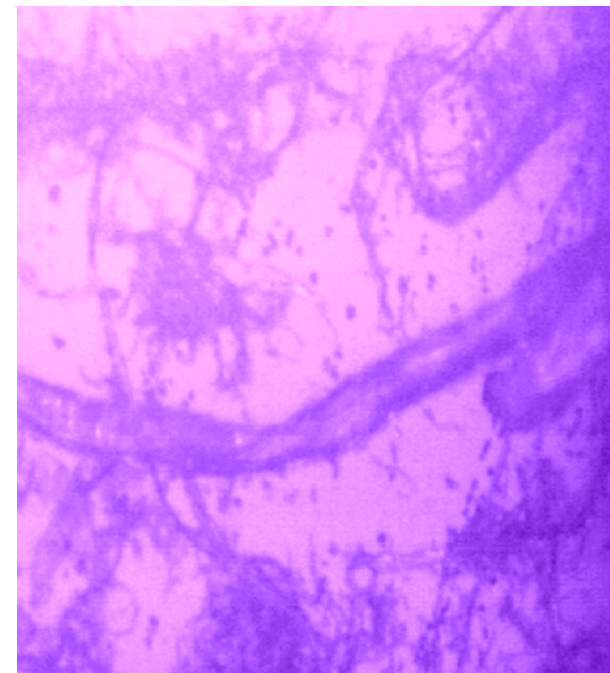
Microscope images of differently degraded papers



Cotton paper

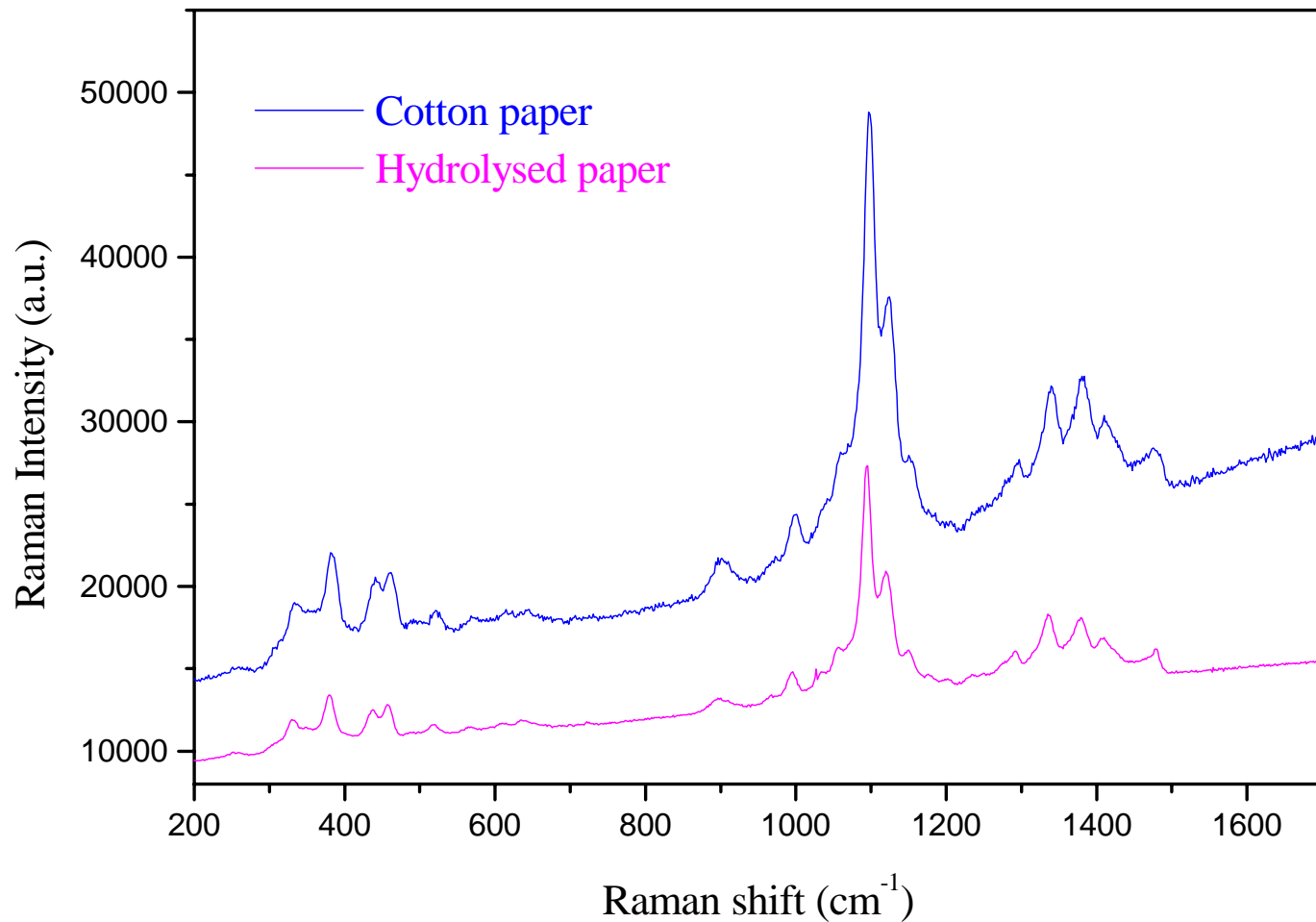


Hydrolysed
paper

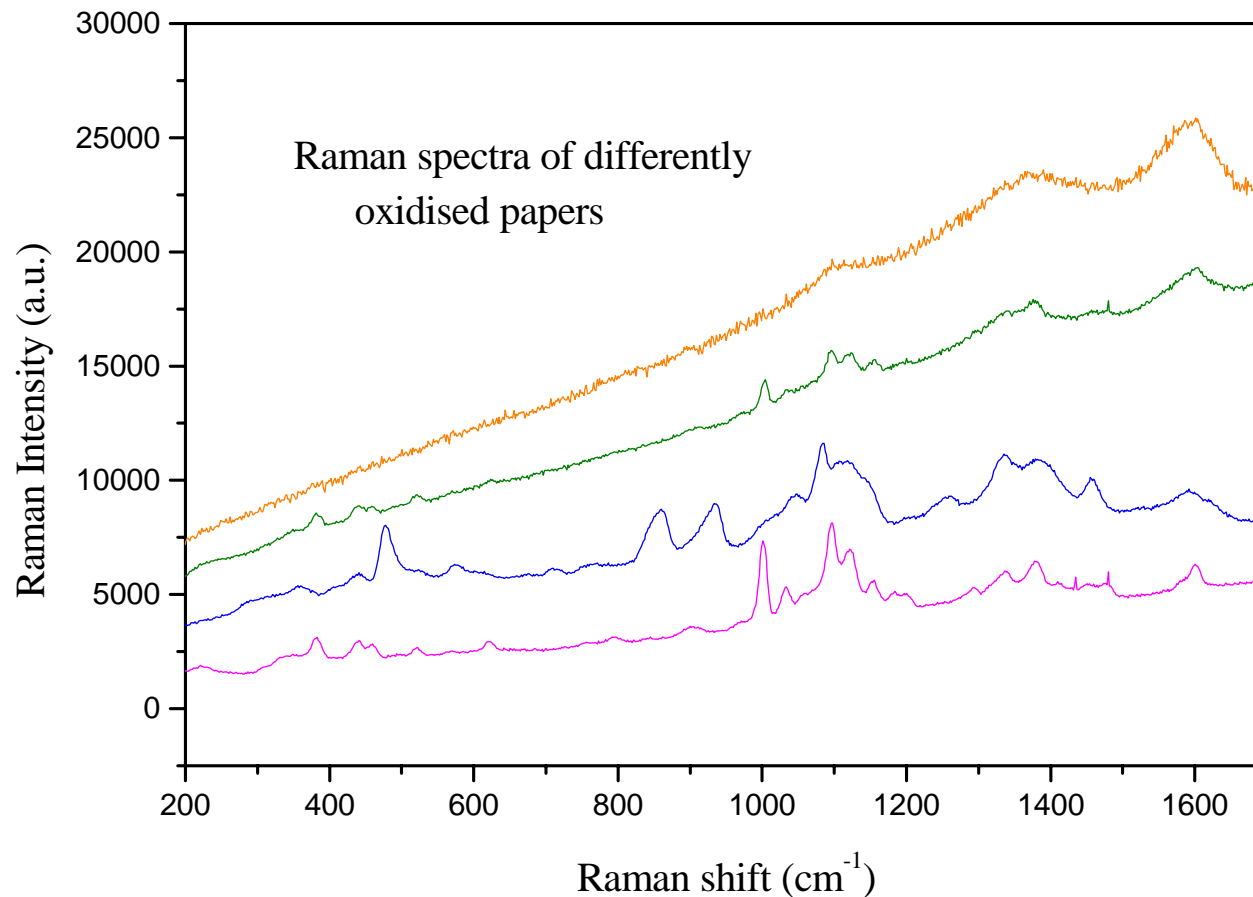


Oxidised
paper

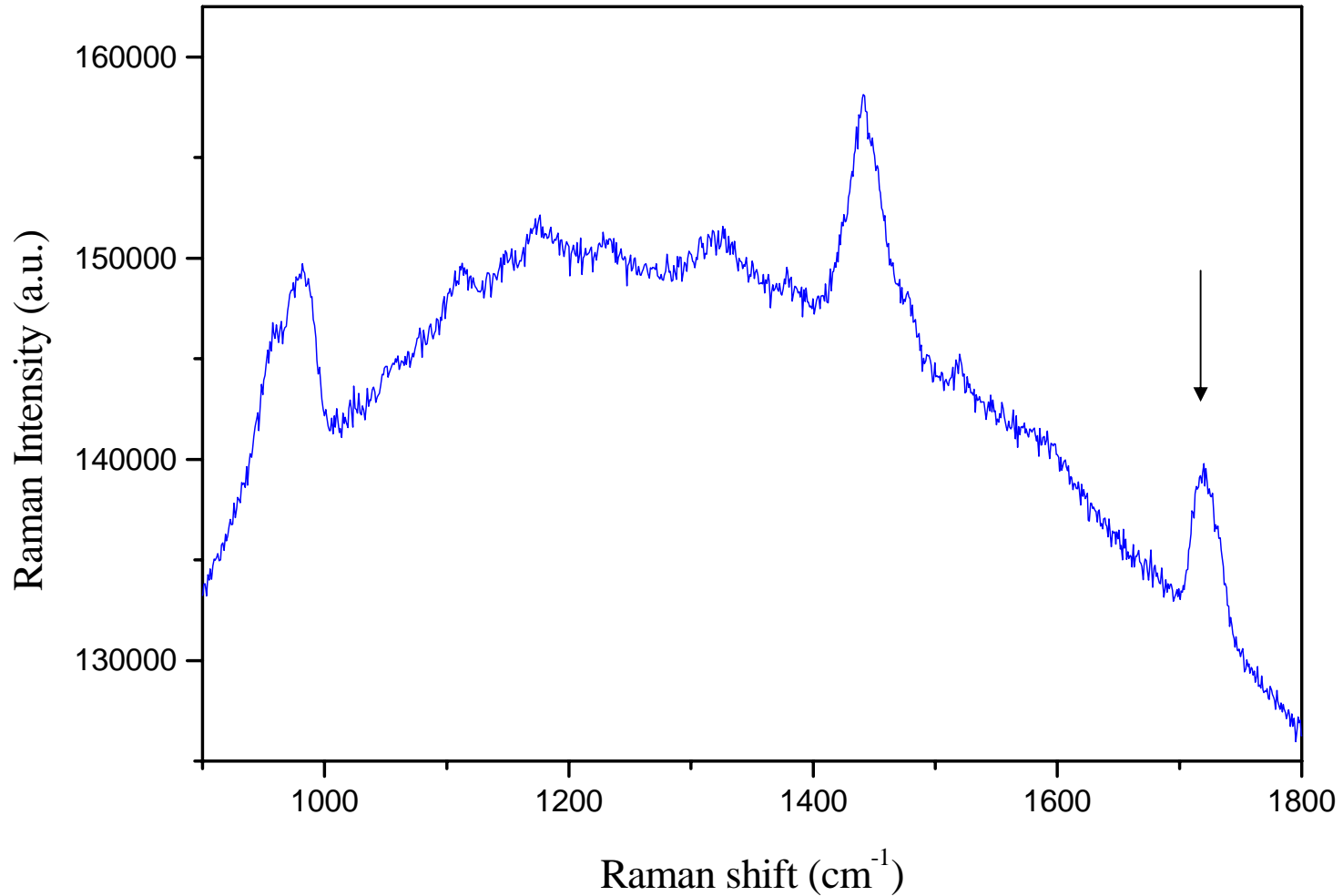
Raman spectra of treated and untreated paper



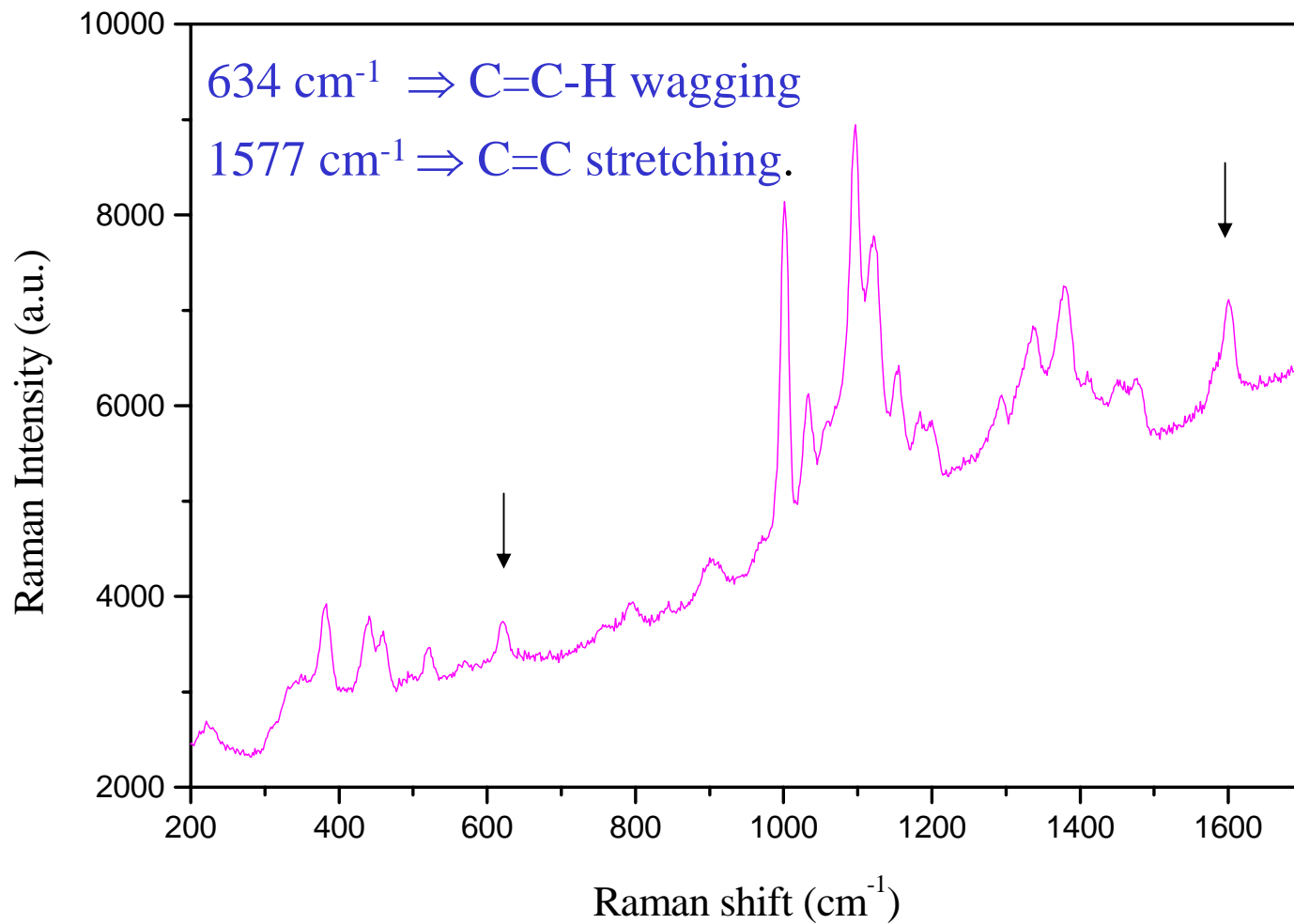
Different samples of oxidised paper that
present a broad peak at 1577 cm^{-1}



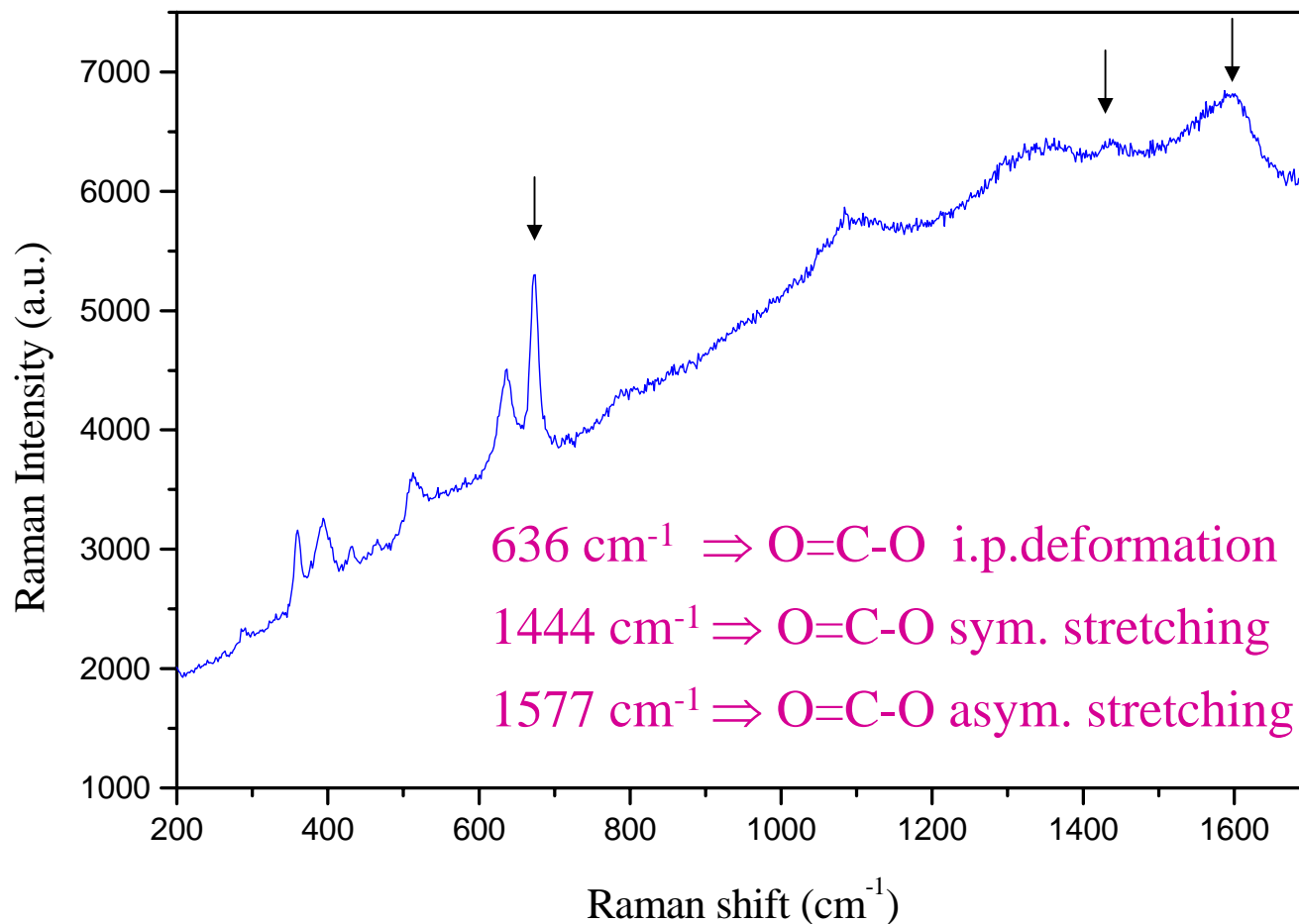
Oxidation to carbonyl groups



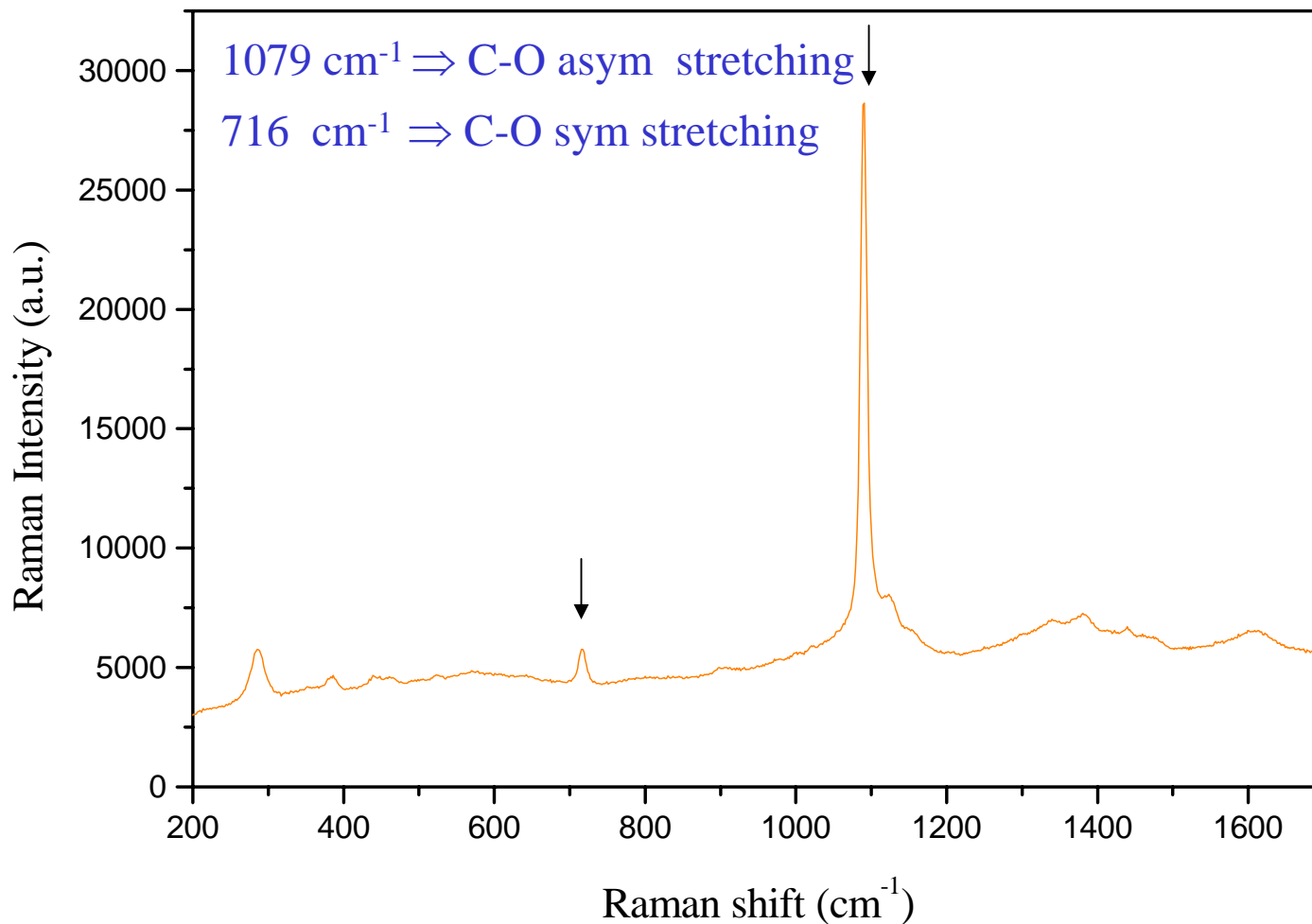
Oxidation to C=C



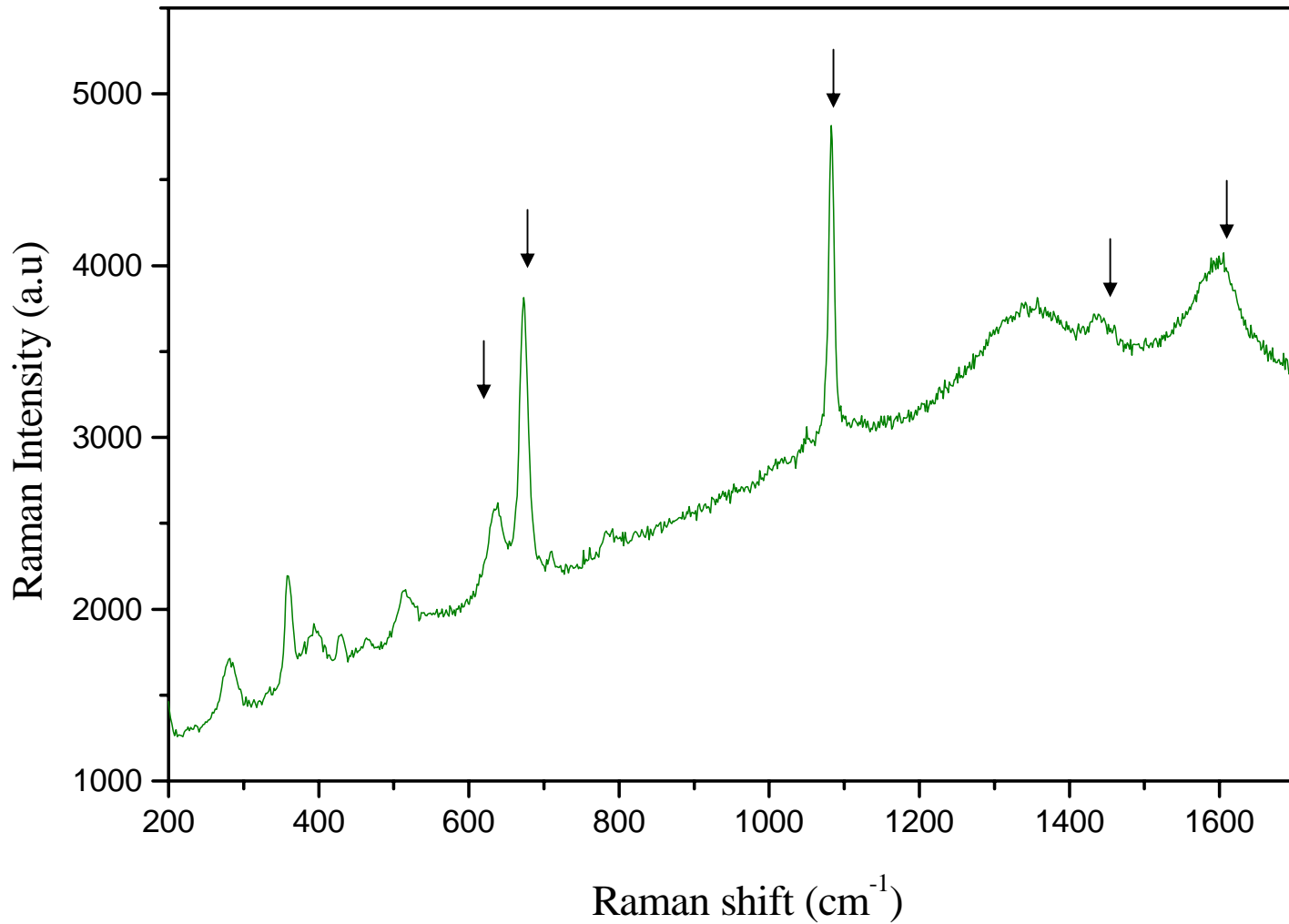
Oxidation to carboxylic groups



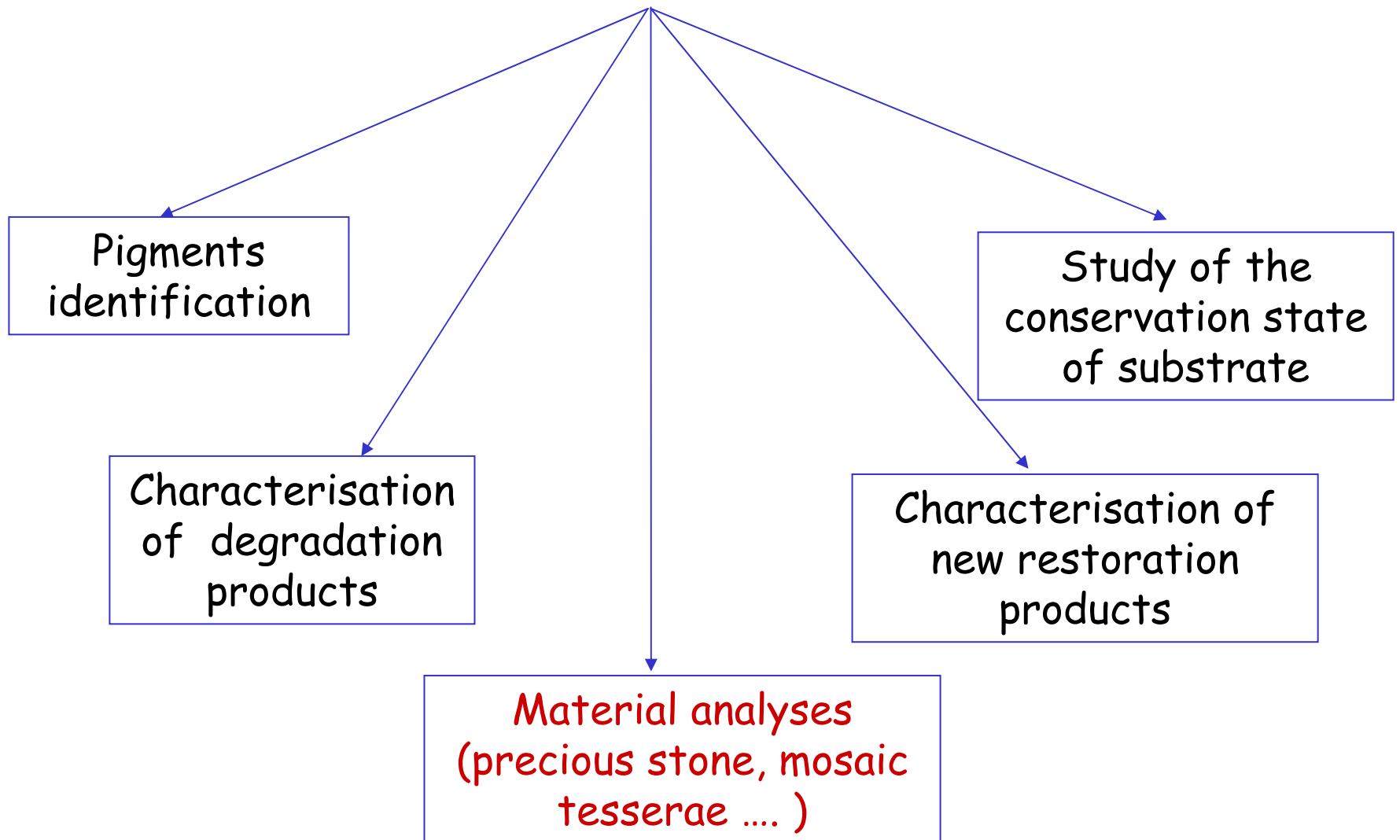
Oxidation to five member cyclic ether



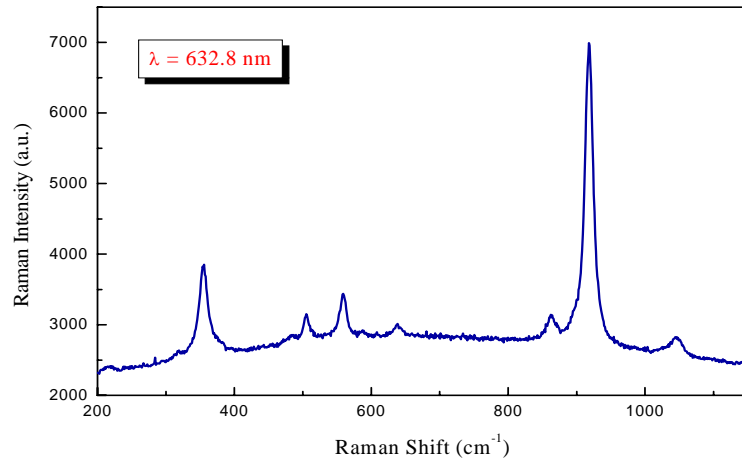
Complex oxidation



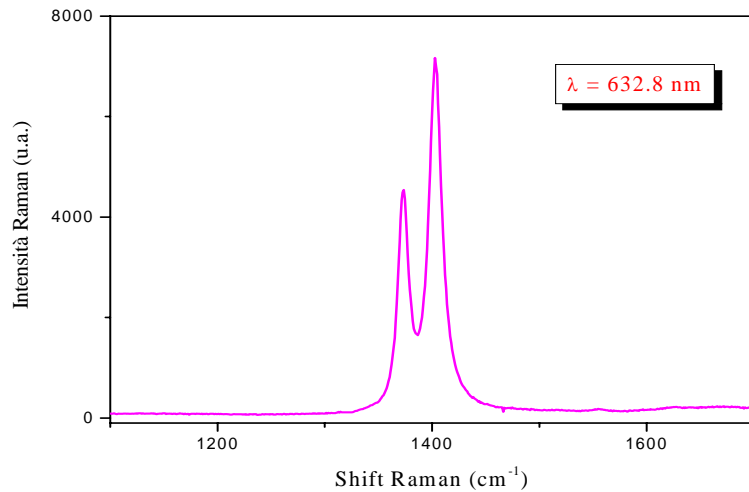
Applications of Raman Spectroscopy to Cultural Heritage



Precious stones identification



SPINEL



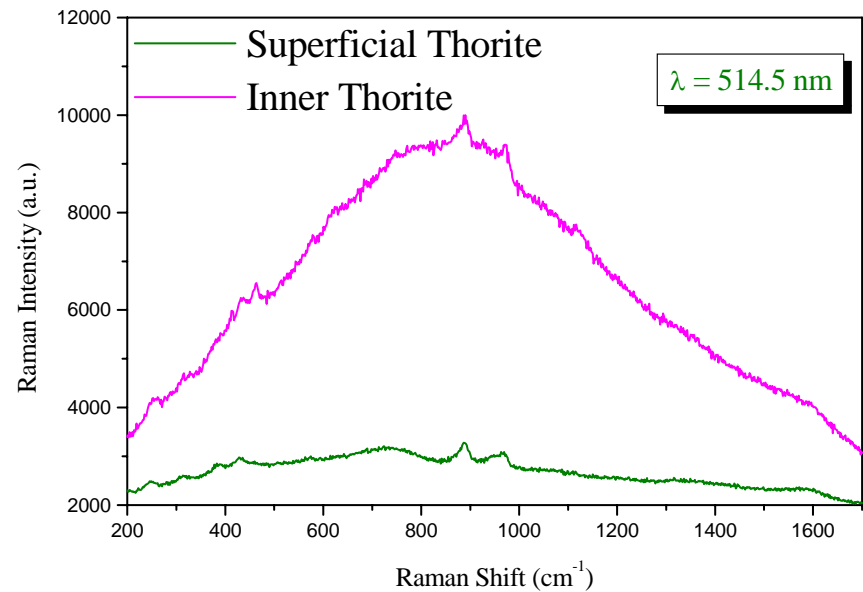
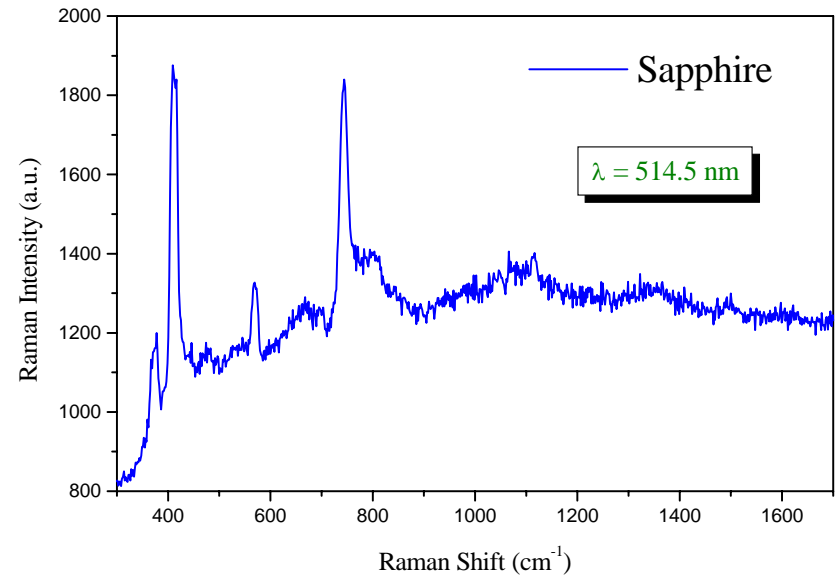
RUBY



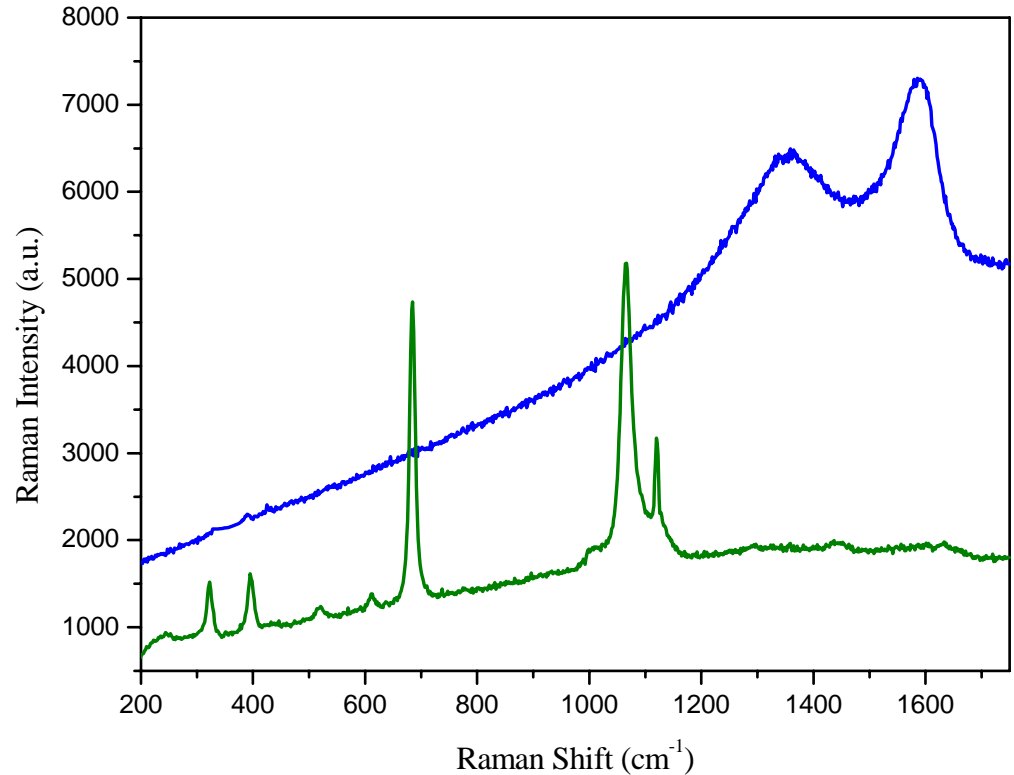
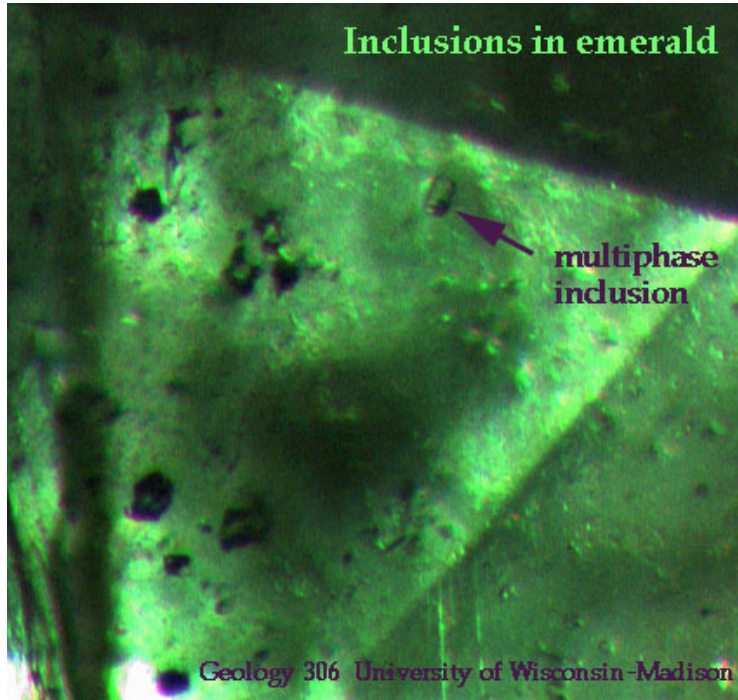
Inclusions study in gems: sapphire



Corundum Al_2O_3

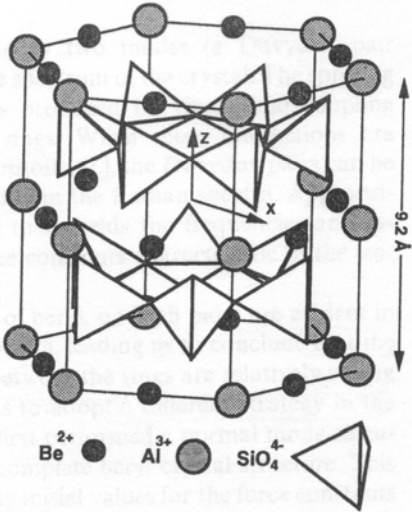


Inclusions study in gems: emerald



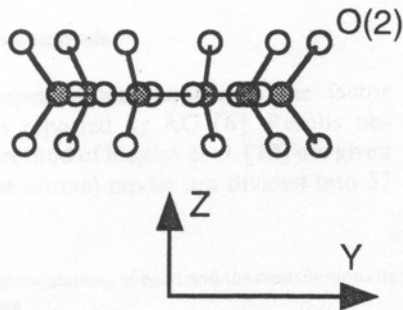
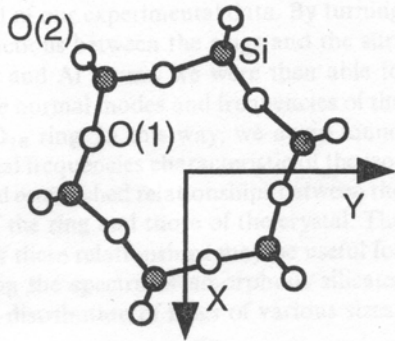
Trapiche (Colombian mine of Muzo)

Beryl provenance identification through vibrational modes study

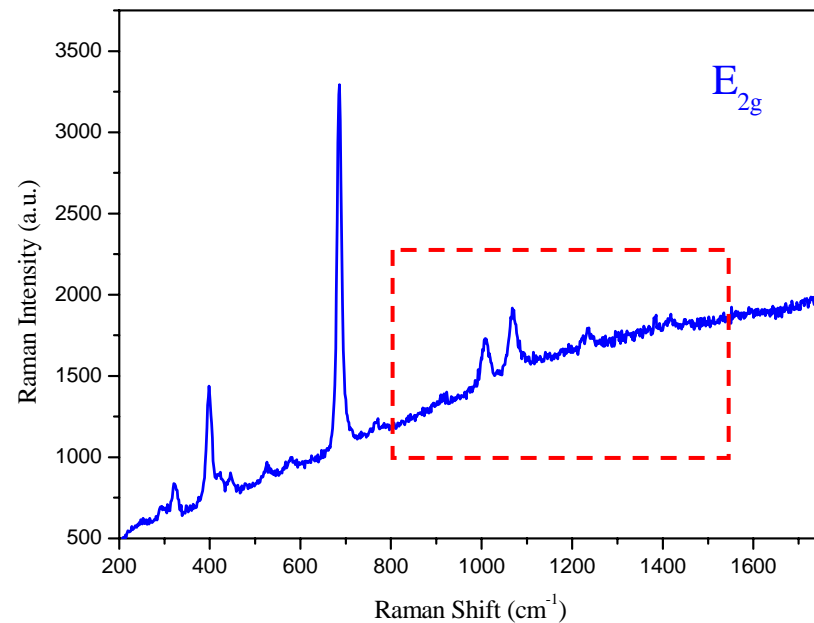
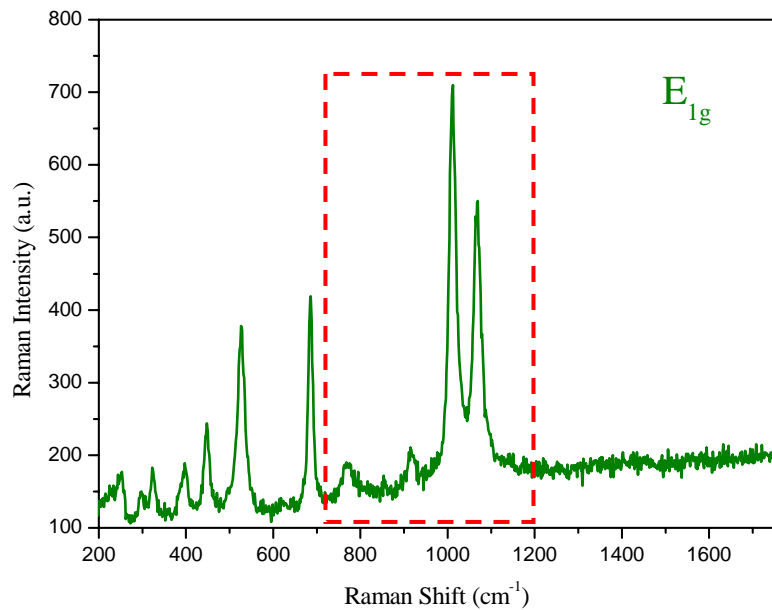
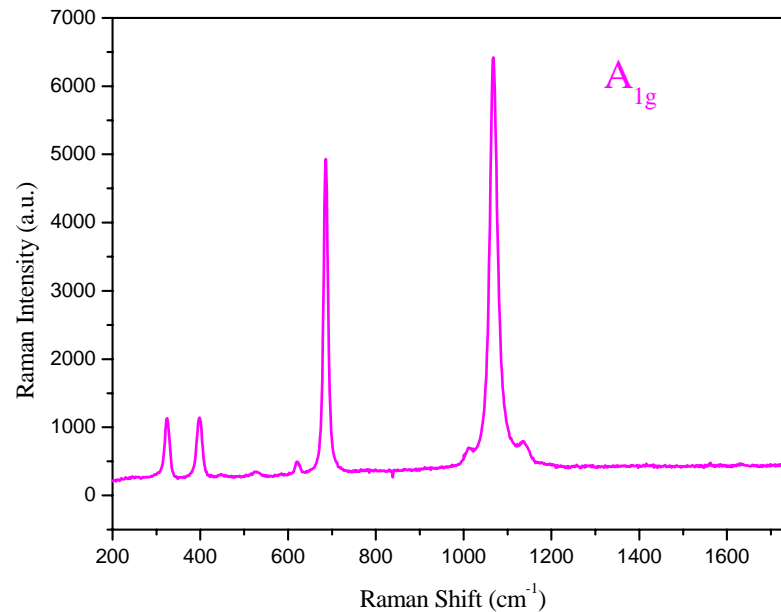


Beryl belongs to space group D_{6h}^{2}

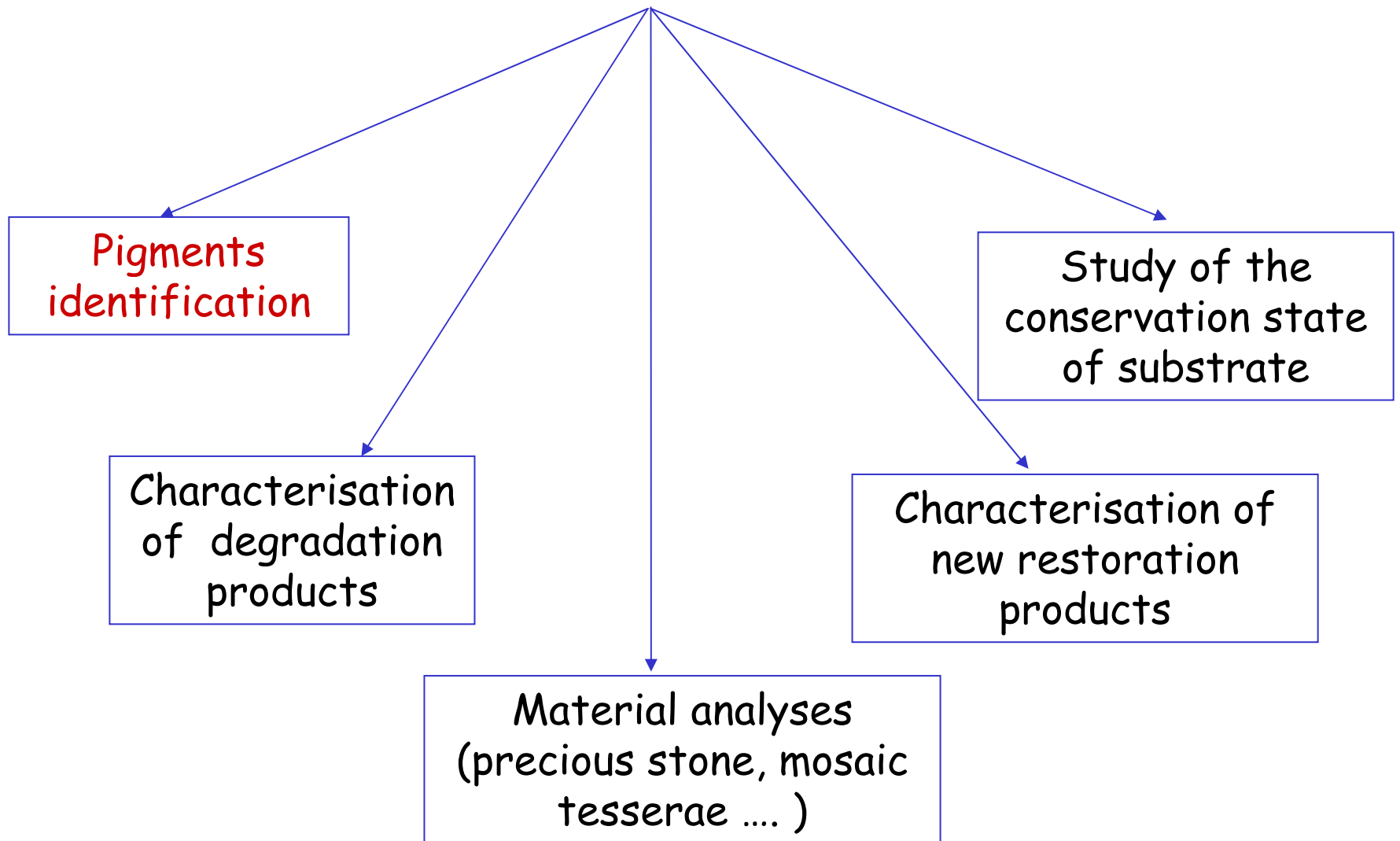
In figure a schematic diagram of the crystal structure of beryl is reported



	A_{1g}	E_{1g}	E_{2g}
n°_{tot}	7	13	16
v_{Si-O}	2	2	4
v_{Be-O}		2	1
v_{Al-O}		1	1
v_{anello}	5	8	10



Applications of Raman Spectroscopy to Cultural Heritage



Works of art analysed for the pigment identification

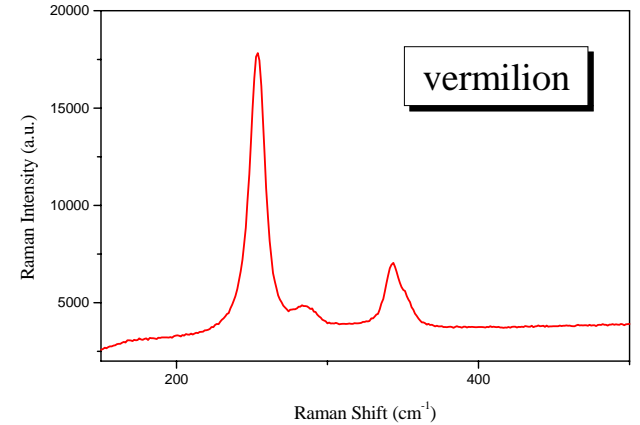
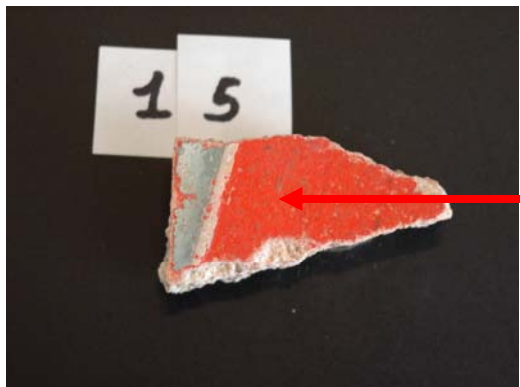
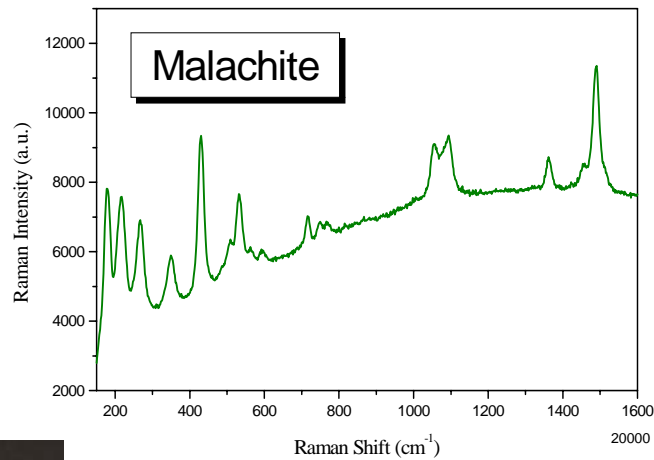
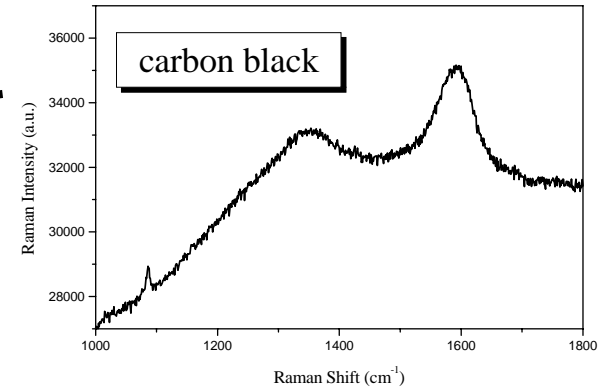
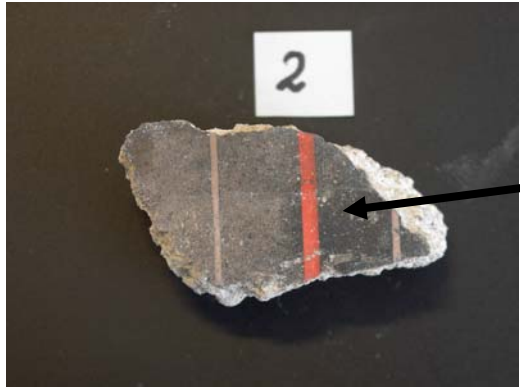
- Illumination attributed to Botticelli (*Il Canzoniere e i Trionfi di F. Petrarca*, manuscript n 143, Biblioteca Classense, Ravenna)
- *Incipit* of Trionfi (Ibidem)
- Stampe colorate a tempera (XVIII sec., collezione del Quirinale)
- **Exultet di Salerno** (XIII sec., Museo Diocesano, Salerno)
- **Bibbia Amiatina** (VII-VIII sec., Biblioteca Laurenziana, Firenze)
- **Frescoes of the "Insula dalle volte dipinte"**, Ostia Antica
- Fresco fragments from Santuario Republicano a Brescia
- Fresco fragments from Tombe di Verghina (Macedonia)
- Fresco fragments from Tombe di Taranto
- Parietal painting fragments from Peruviane
- Fresco fragments from **studiolo della Domus Augustea** (Palatino)
- Painted ceramic fragments (Middle Age, from Miseno)
- Parietal painting fragments from the "*Red Convent*" (VI sec. Sohag, Egitto)

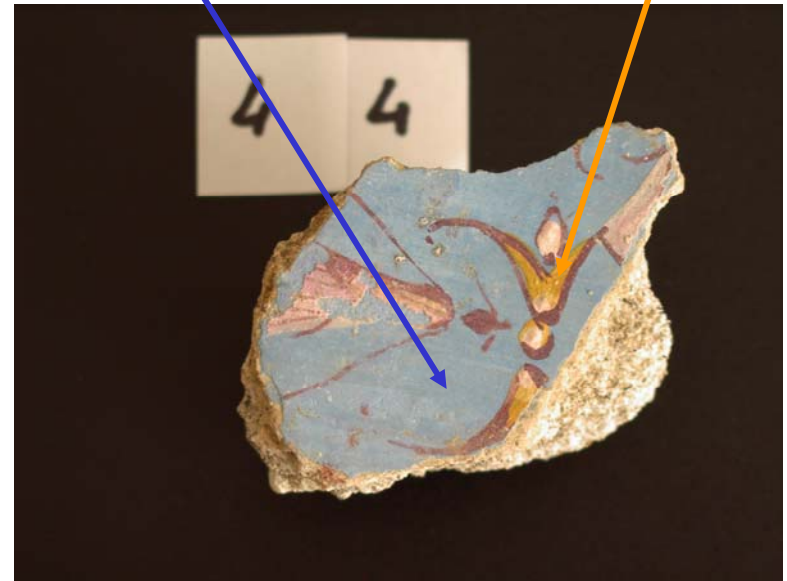
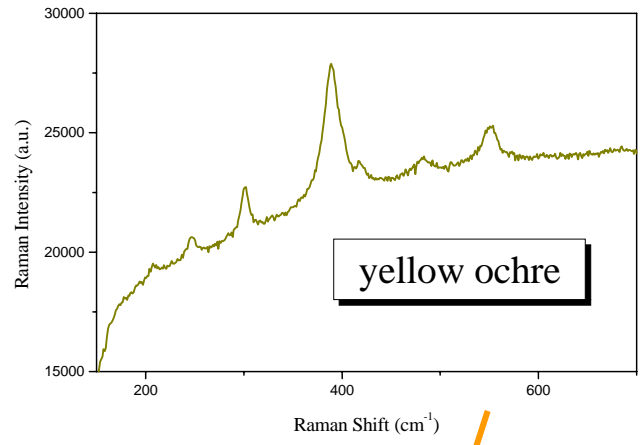
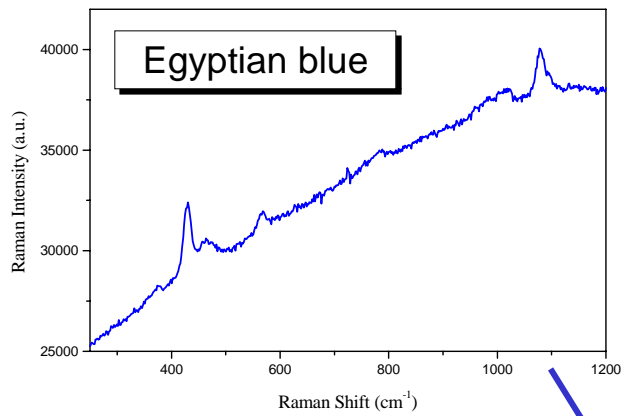
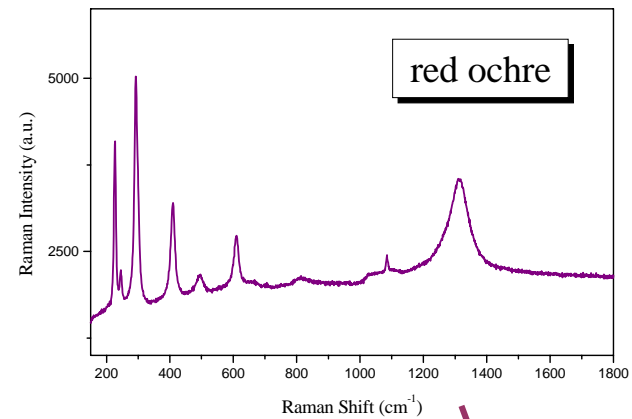
STUDIOLO di AUGUSTO

Domus Augustea al Palatino- Roma



STUDIOLO - DOMUS AUGUSTEA





All the pigments were identified using ONLY the Raman technique

What is an Exultet?

The Exultet is an illustrated parchment scroll coming from Southern Italy. The name comes from the word that begins the prayer of benediction of the Easter candle: "Exultet iam angelica turba coelorum". This prayer is written on the parchment and read on the night before Easter.

The Exultet were made in order to lend the greatest solemnity to the celebration of Easter services.

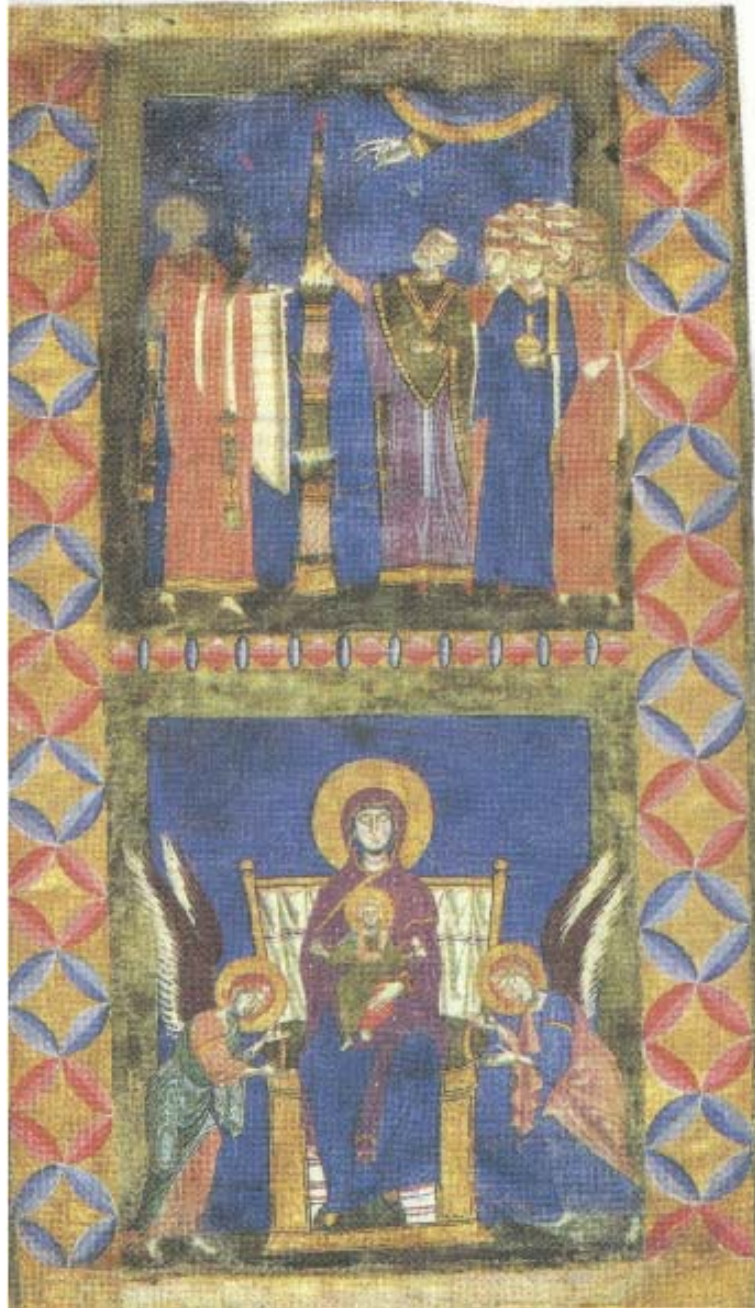
They were carefully decorated with musical annotations, heads and several miniatures. The images serve to illustrate the prayers that were recited by the deacon from the pulpit: liturgical scenes, episodes from the Old and New Testaments, and scenes of contemporary life.



The Salerno Exultet

The Salerno Exultet is a parchment roll about eight-metres long. It is very different from other Exultet, in fact it is fully decorated and only the first fragment contains a text.

The Salerno Exultet was produced between 1225 and 1227 and it is the work of two artists.



The Salerno Exultet: the analysed sections



Section I



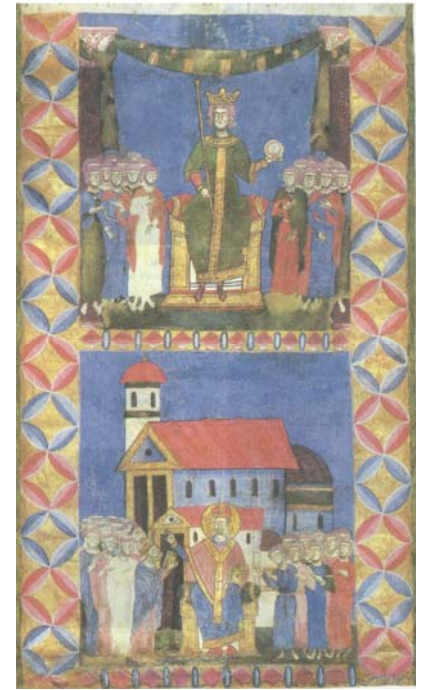
Section II



Section VII



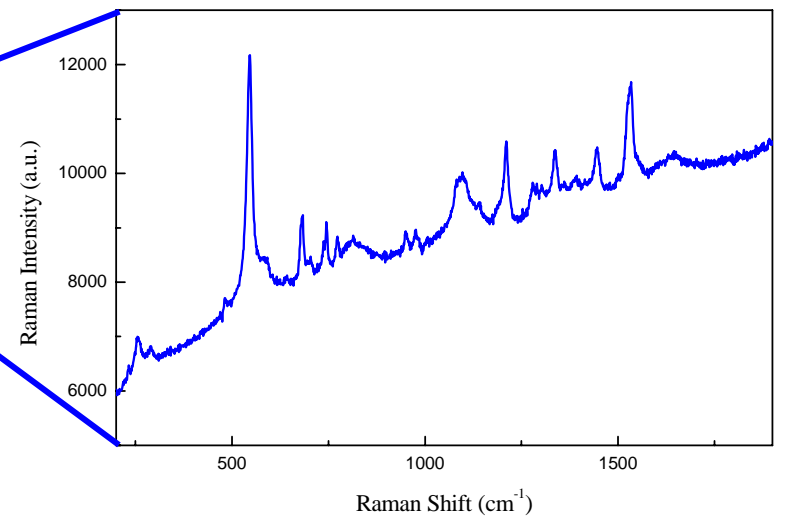
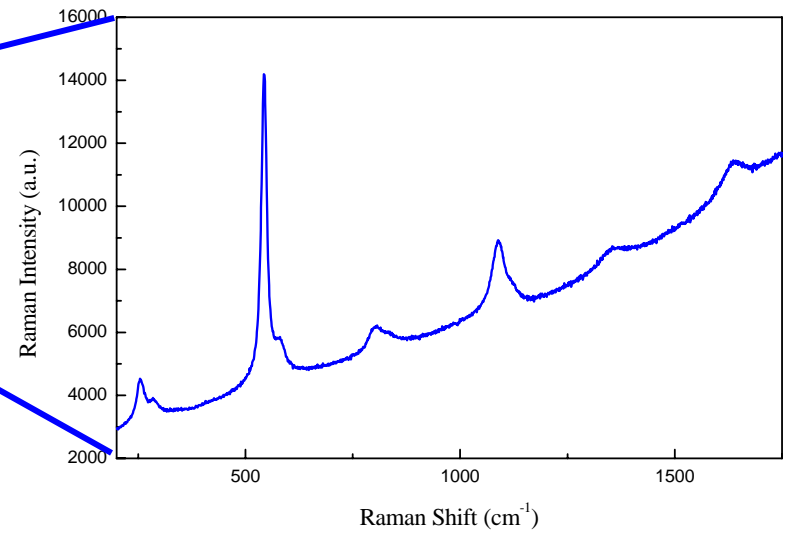
Section X



Section XI

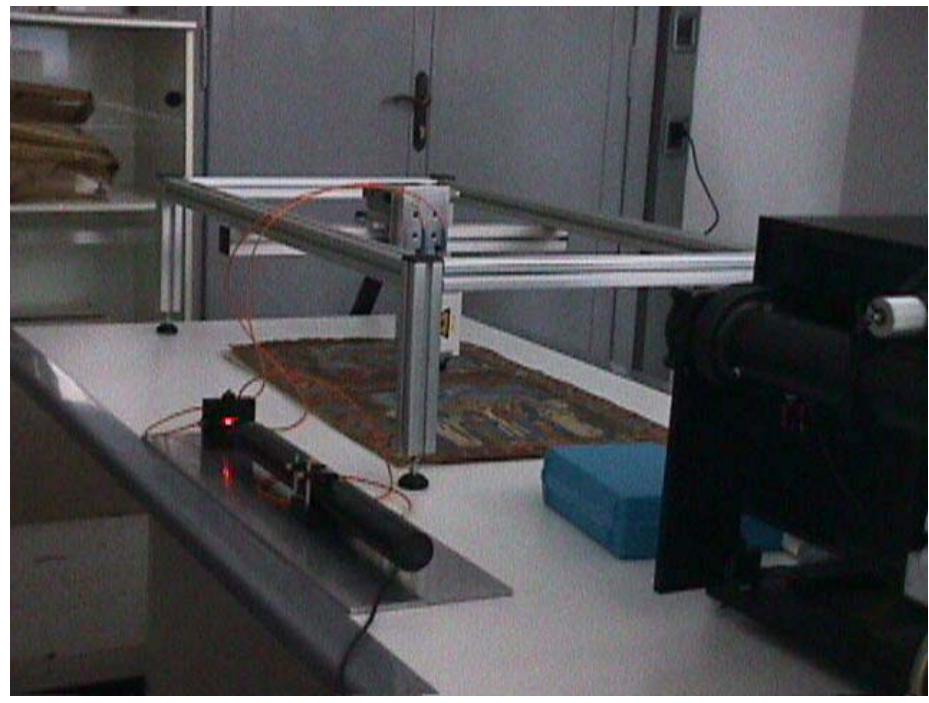
Results:

the blue pigment

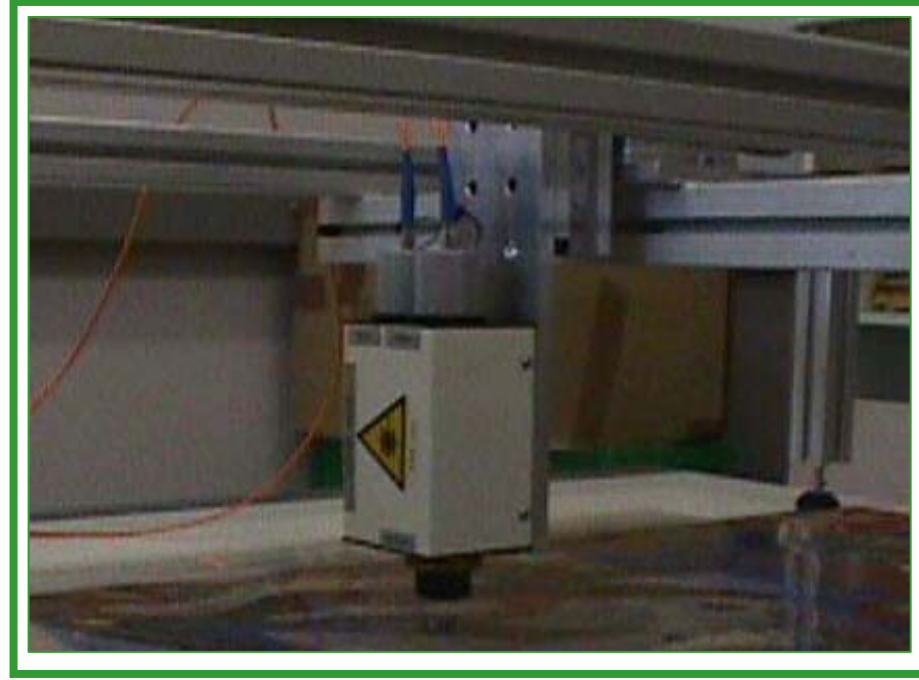






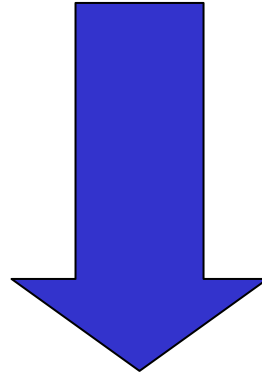


← Optical fiber measurement head



Optical fiber measurement head →

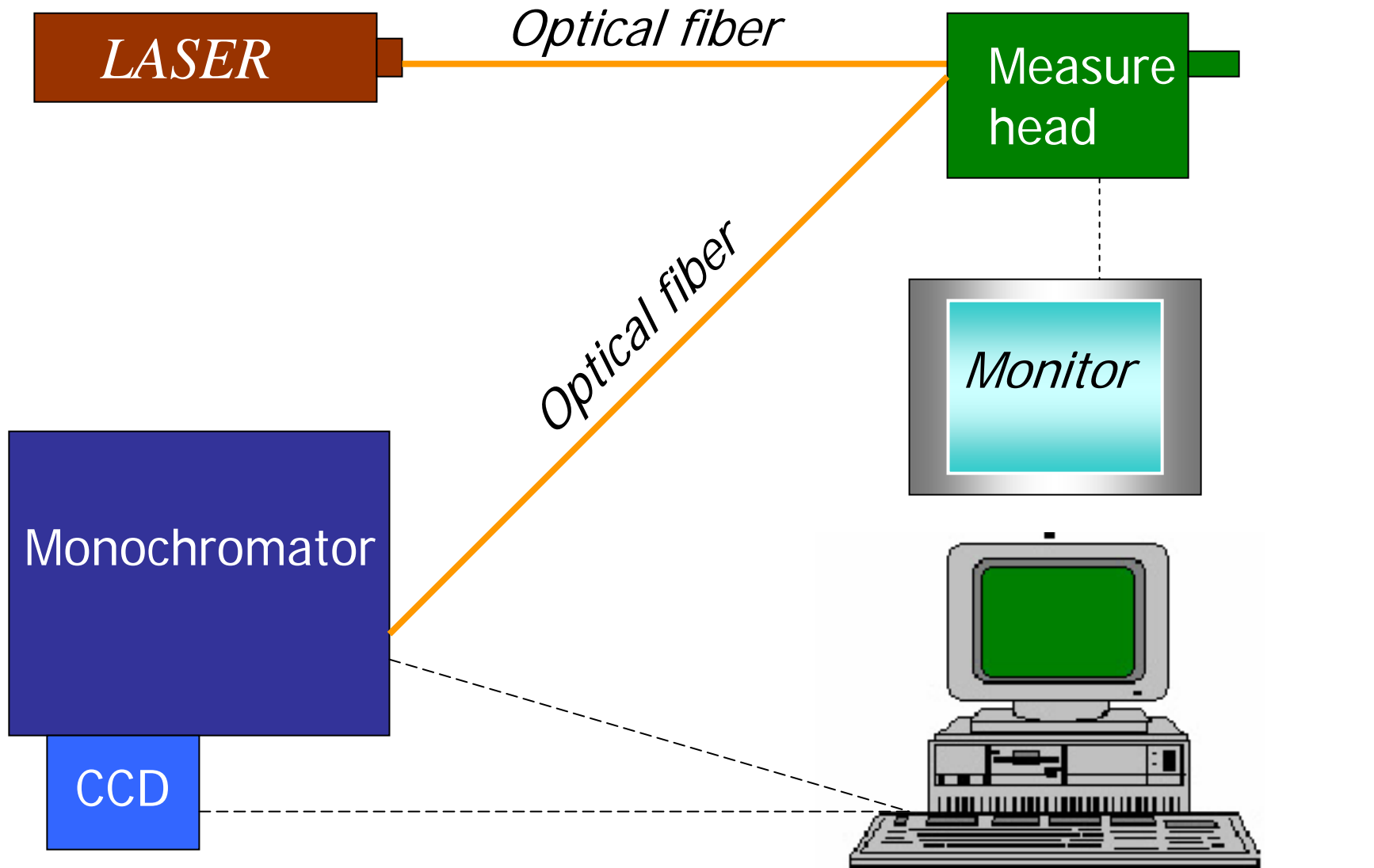
owing to their dimension or their high intrinsic value many pieces of art cannot be brought to our laboratory for analysing



PORTABLE RAMAN SYSTEM

Requirements for Cultural Heritage applications

- different LASER sources easily interchangeable
- a system to illuminate the sample and collect the scattered light based on optical fibres
- a dispersion monochromator with interchangeable gratings to cope adequately with the different resolution and spectral range required by the sample nature and by the LASER adopted
- good spectral resolution
- a micrometric precision for both positioning and spatial resolution of the sampling
- visualisation of the exact measurements point
- a specific software to control the system electronics and the data acquisition



Computer to control the monochromator and CCD and to analyse data

Portable custom-made Raman System



2 LASER sources (514.5 and 632.8 nm)

Via optical fibres two distinct measuring heads are connected to the source and to the monochromator

These heads are mounted on a metal frame which allows micrometric x-y-z positioning.

A removable beam splitter allows the insertion of video-camera for observation of the exact points in which the measurements are performed.

The monochromator is a Jobin-Yvon TRIAX 320 mm focal length equipped with three interchangeable gratings (150, 1200 and 1800 groves /mm) which allows an ultimate resolution better than 1 cm^{-1} in the visible.

A cooled CCD detector (1024 x 256 pixel)

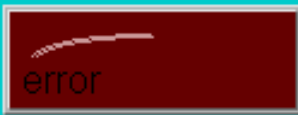
Configurazione

Calibrazione

Acquisizione

EXIT

ACTUAL VALUE



SETTING VALUE

wavelength (nm)

0.00

SET

wavelength (nm)

0.00

slits

0.00

SET

slits

0.00

Turret

grid 1200

SET

Turret

grid 1200

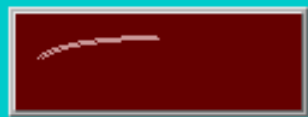
Entrance Mirror Pos

AXIAL

Entrance Mirror Pos

AXIAL

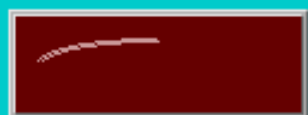
INIT OK MONO



PMA SETUP

INIT

INIT OK PMA



EXIT CONFIG

Comparison between our portable Raman system and the ones now in commerce



InPhotote - InPhotonics



Sentinel - Chromex



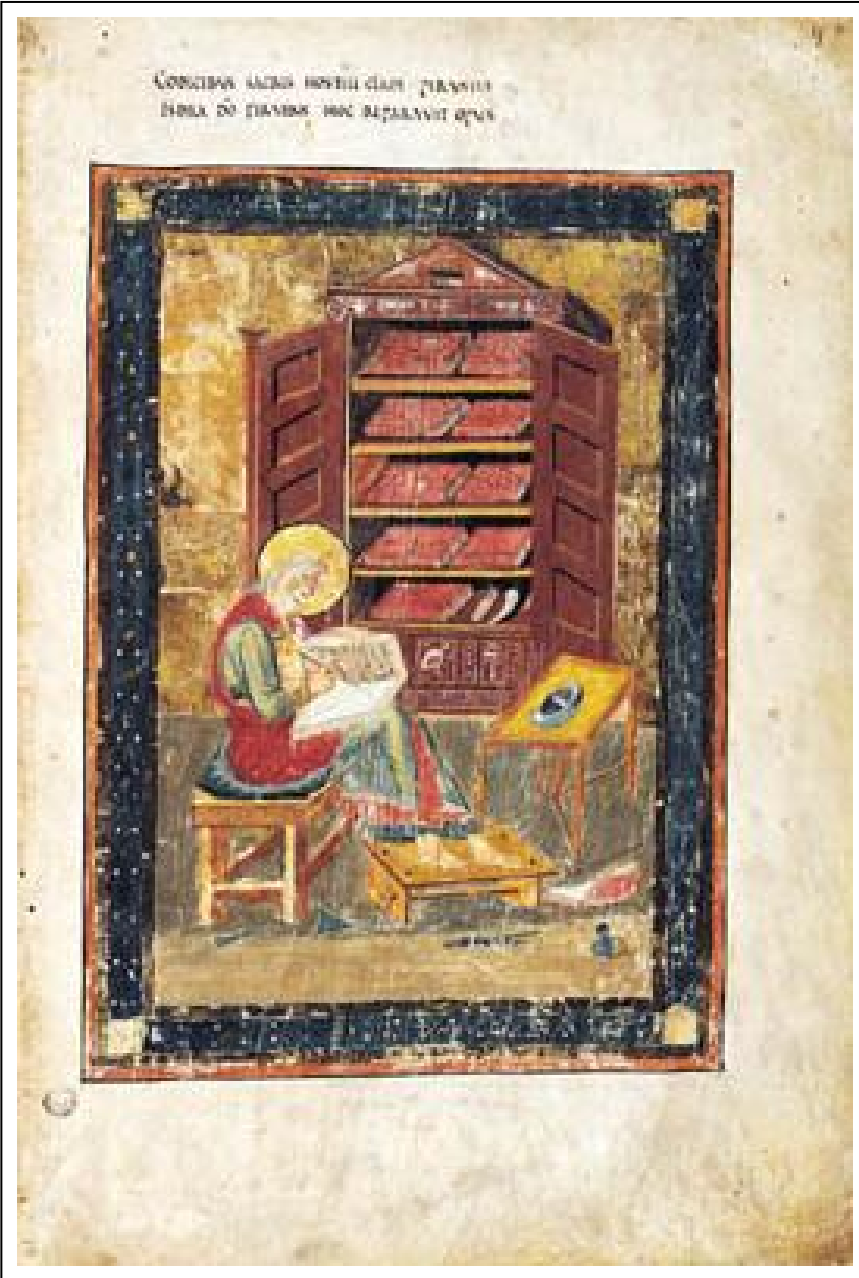
Solution 633 - Detection Limit



R-2001 - Ocean Optics

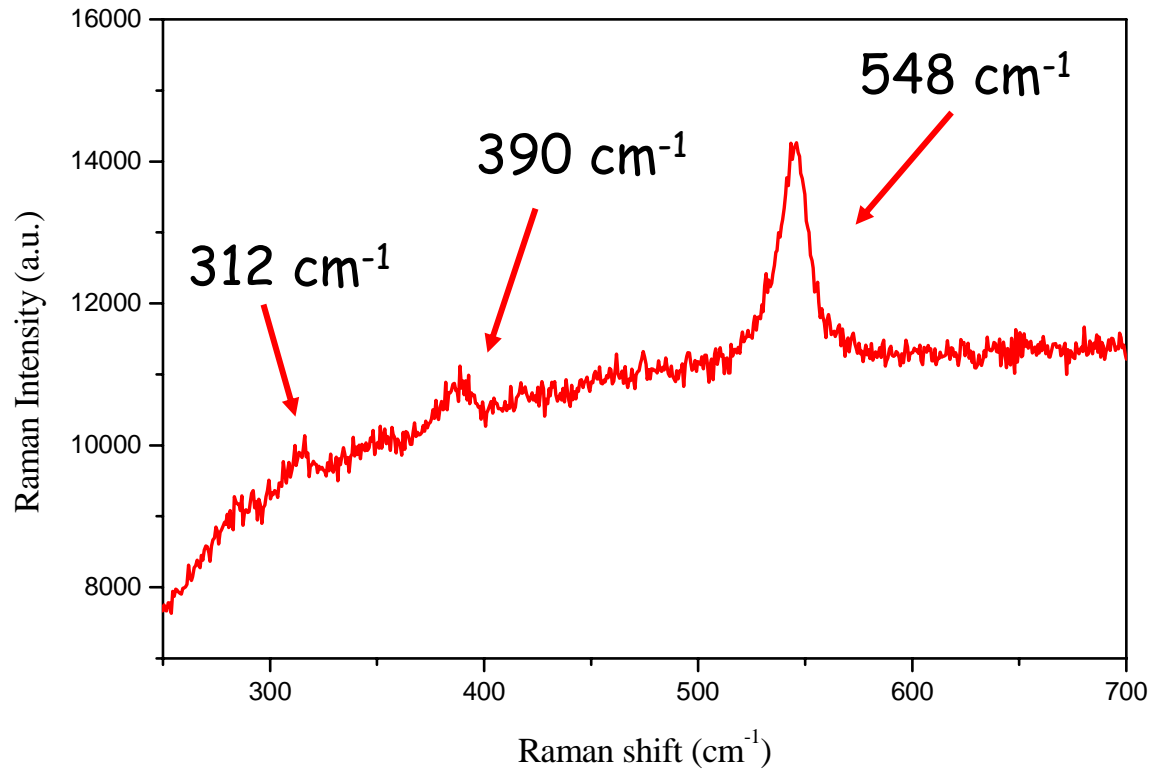
	<i>InPhotote</i>	<i>Sentinel</i>	<i>Solution 633</i>	<i>R-2001</i>	<i>Our portable Raman system</i>
Resolution (cm ⁻¹)	6	6	7	15	< 1
Range (cm ⁻¹)	200-1800	200-2000	250-3600	200-2700	200-3600
Laser source	785 nm diode laser 300 mW	810 nm diode laser 70 mW	633 nm He-Ne laser 30 mW	785 nm diode laser 500 mW	633 nm He-Ne 30mW
					514 nm Ar ⁺ 300 mW
Optic Fibre measurement head	yes: with 5 meter fibre	yes: with 3 meter fibre	yes: with 2 meter fibre	yes: with 10 meter fibre	yes: with 5 meter fibre
Working distance	5 mm	2 o 50 mm		2-7 mm	From 2 mm to 2.1 cm
Presence of a camera	NO	NO	NO	NO	YES
Dimension (cm)	41 x 25 x 23	38 x 46 x 20	33 x 18 x 23	28 x 20 x 8	92 x 68 x 74.5
Weight (kg)	9	13	< 9	3	45 (trolley included)
Cost (k €)	50	65	25	13	38

The "*Bibbia Amiatina*"



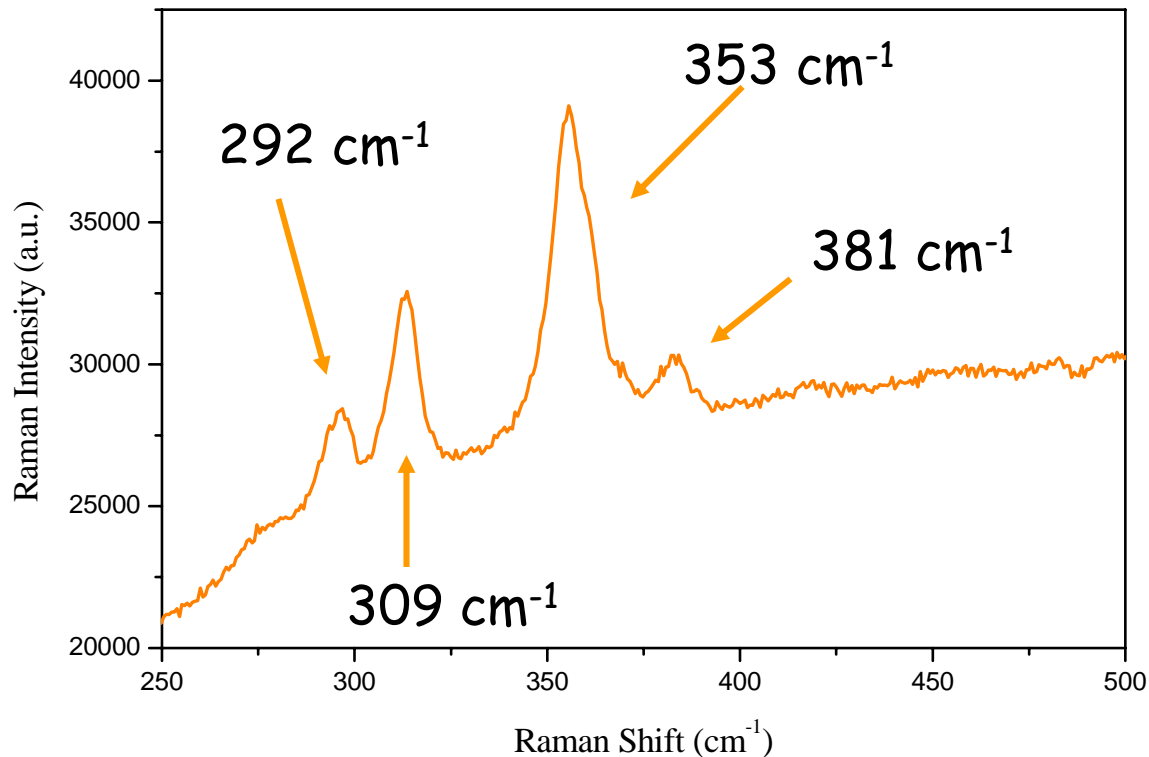
- The *Bibbia Amiatina* is an ancient codex and its dimensions are 500x335 mm
- It dates back between the end of the VII and the beginning of the VIII century
- It was produced in the monastery of Wearmouth-Jarrow in England together with other two manuscripts of which only few fragments are available
- Only the first eight sheets of this codex and the page that separate the Old and the New Testament are richly decorated

First results obtained with the portable Raman system:



Red zone → red lead

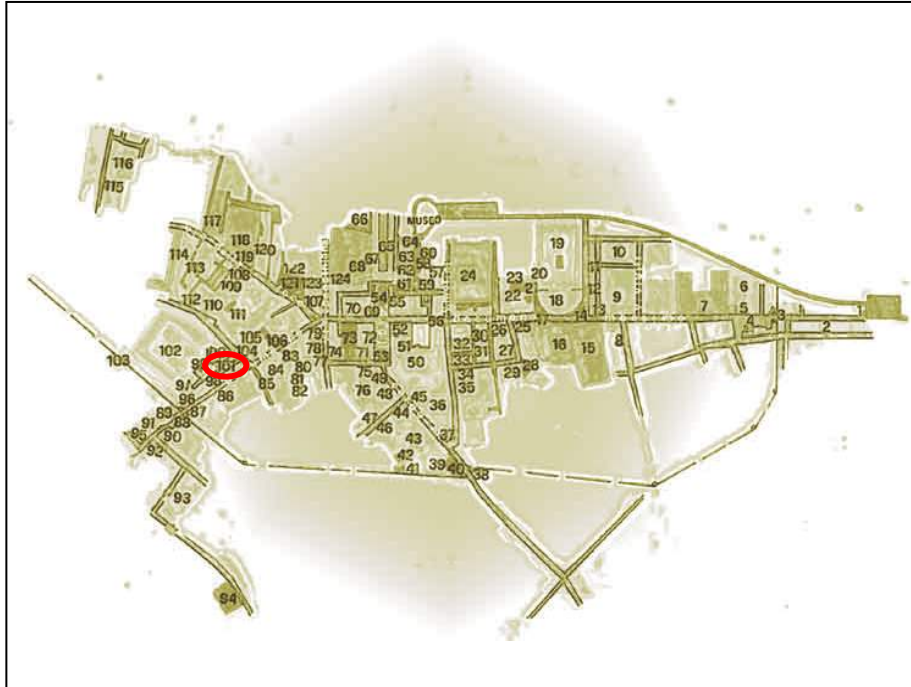
First results obtained with the portable Raman system:



Yellow zone → orpiment

The pigment identification contributed to the determination of the lost progressive page numeration

Insula dalle volte dipinte – Ostia Antica



Internal frescoes of the Insula



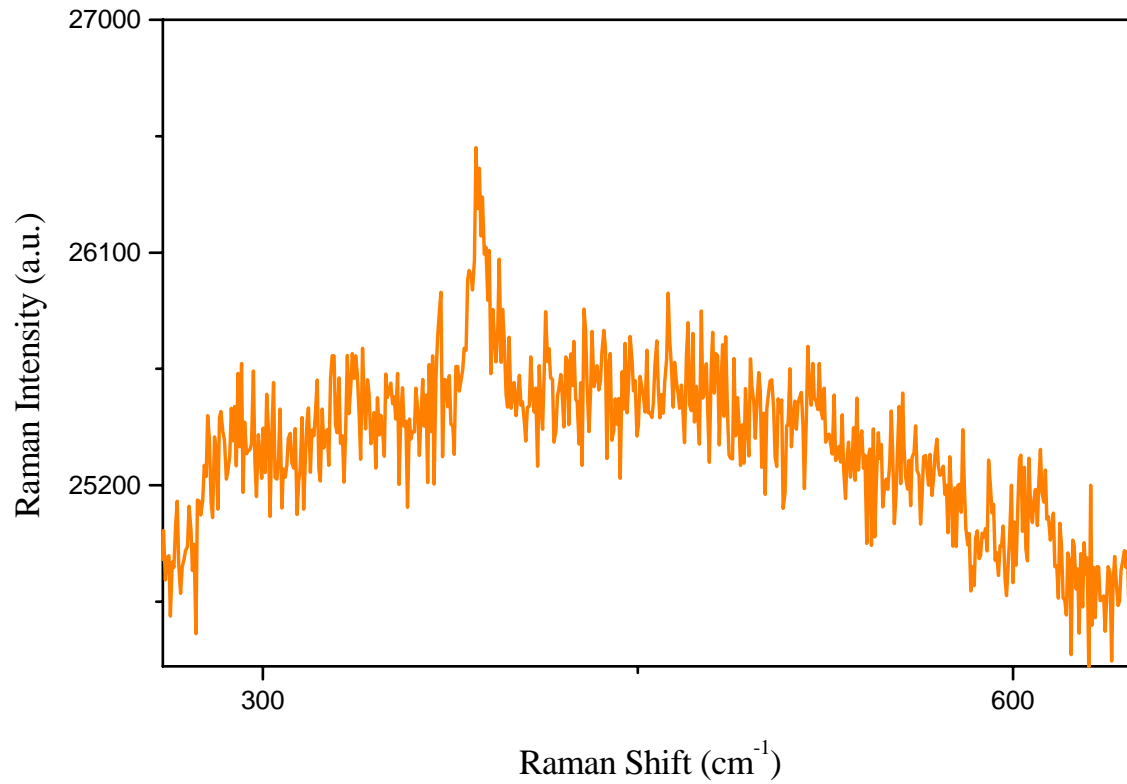
Wall fresco



Vault fresco

Portable Raman system during the measurements





Yellow zone



yellow earths

Conclusions

- Raman spectroscopy is revealed as a useful technique to identify pigments, to study the degradation processes and to analyse several materials.
- Since not all the works of art can be moved to our laboratory, it was necessary to set up a portable Raman system
- The portable Raman system was characterised and it showed a remarkable versatility and performance comparable to the new generation laboratory system
- The portable Raman system was successfully employed to analyse the *Bibbia Amiatina* and the frescoes of the *Insula dalle Volte Dipinte*

Church of S. Bishoi
Red Convent- Sohag - Egypt

