Infrared & Raman Users Group

Raman Spectroscopy Workshop

Philadelphia Museum of Art

September 27 – 28, 2012

Support for the workshop provided by:

NCPTT

INSTITUTE of Museum and Library SERVICES

BRUKER

FDM
Fiveash Data Management, Inc.

DOW

V&A

NATIONAL GALLERY OF ART U.S.A.

IFAC

IRUG

Philadelphia Museum of Art

Benjamin Franklin Parkway at 26th Street, Philadelphia, PA 19101-7646
www.philamuseum.org

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Welcome and opening remarks

Beth Price, Senior Scientist

Timothy Rub, The George D. Widener Director and CEO

Andrew Lins, The Neubauer Chair of Conservation

Philadelphia Museum of Art, US

THURSDAY, SEPTEMBER 27: WELCOME & OPENING

What is IRUG?

An independent, not-for-profit corporation of individuals who use IR and Raman spectroscopy to study the world’s cultural heritage

IRUG Board of Directors

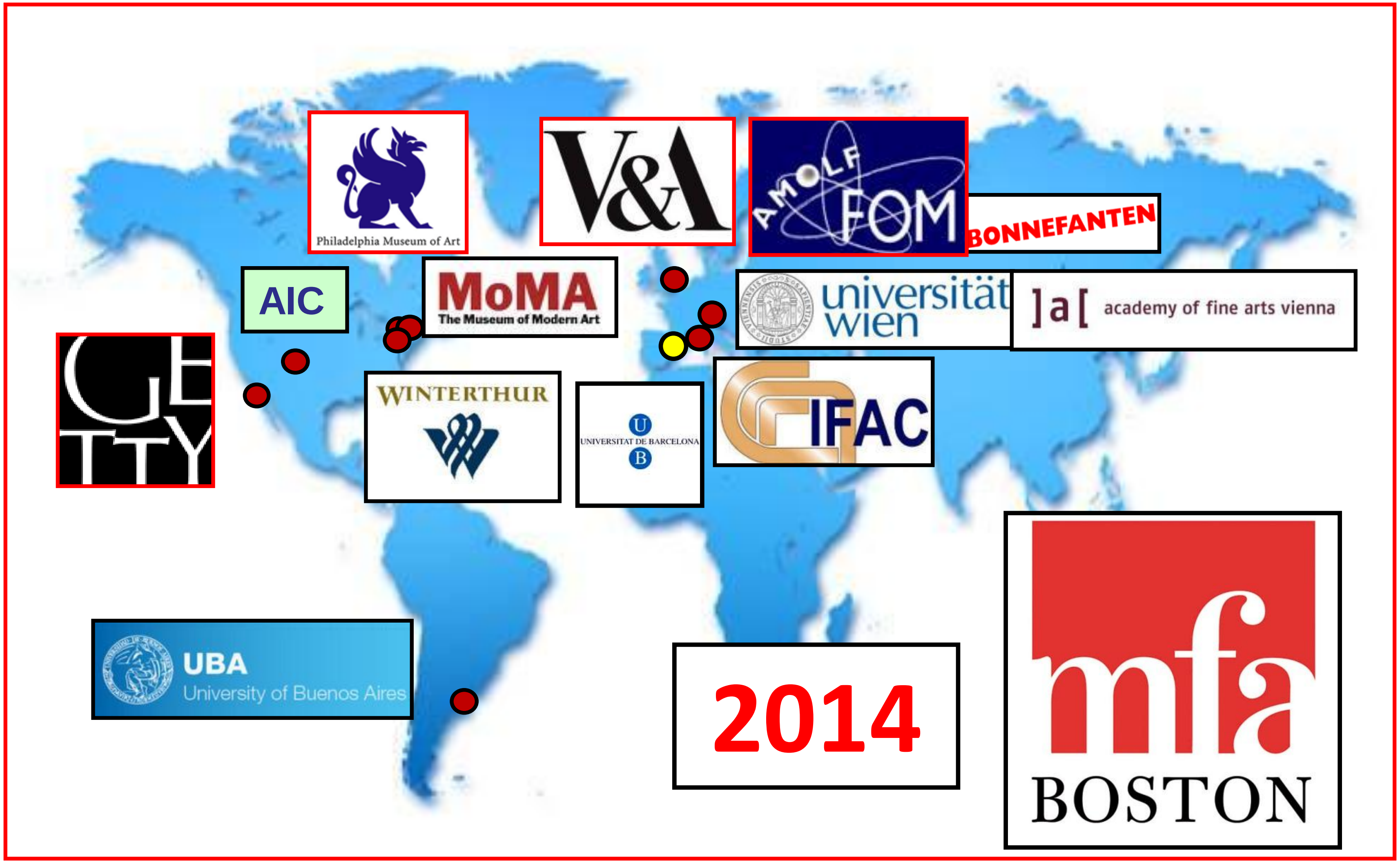
Herant Khanjian	Getty Conservation Institute
Suzanne Lomax	National Gallery of Art, Washington
Marta Maier	University of Buenos Aires
Richard Newman	Museum of Fine Arts, Boston
Marcello Picollo	IFAC Nello Carrara, CNR
Boris Pretzel	Victoria & Albert Museum
Beth Price	Philadelphia Museum of Art
Manfred Schreiner	Academy of Fine Arts, Vienna
David Thickett	English Heritage
Scott Williams	Canadian Conservation Institute
Masanori Sato *	Nara Cultural Research Institute
Raymond White *	National Gallery, London

* Retired, honorary Board members

IRUG Mission

To improve, expand & distribute the IR & Raman data shared by its members.

Biennial Conferences 1994 – 2012

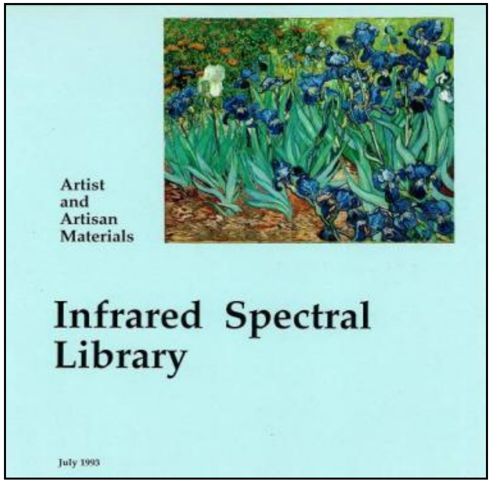


IRUG Databases 1993-2009

1993

777 spectra

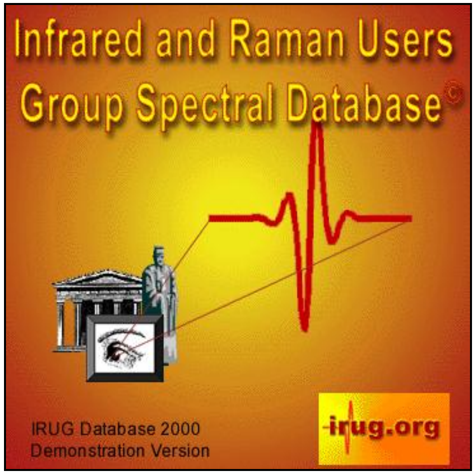
9 institutions



Artist
and
Artisan
Materials

Infrared Spectral
Library

July 1993



Infrared and Raman Users
Group Spectral Database©

IRUG Database 2000
Demonstration Version

irug.org

2002

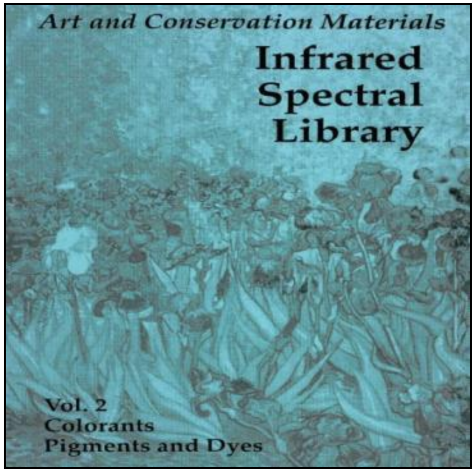
1254 spectra

100 institutions

1994-5

1259 spectra

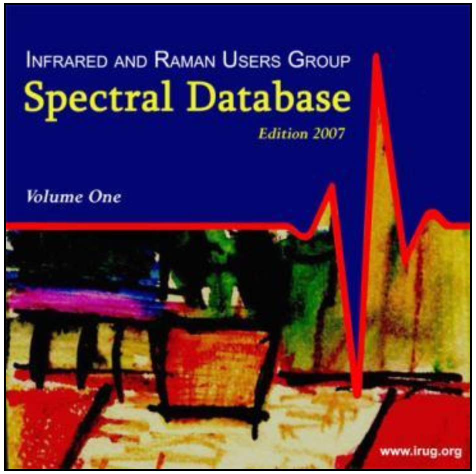
21 institutions



Art and Conservation Materials

Infrared
Spectral
Library

Vol. 2
Colorants
Pigments and Dyes



Infrared and Raman Users Group

Spectral Database

Edition 2007

Volume One

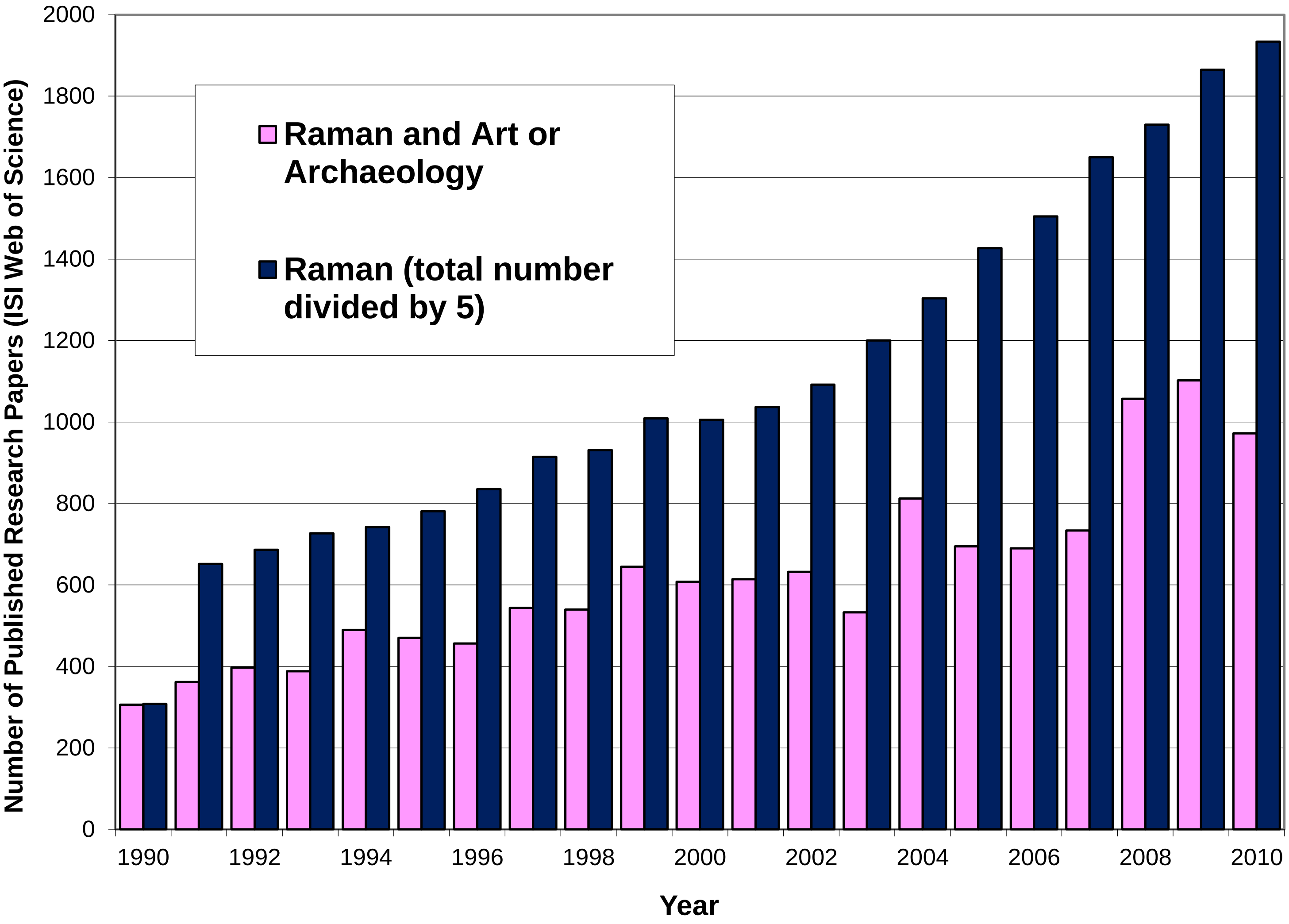
www.irug.org

2009

2,128 spectra

100+ institutions

Raman Papers Have Risen

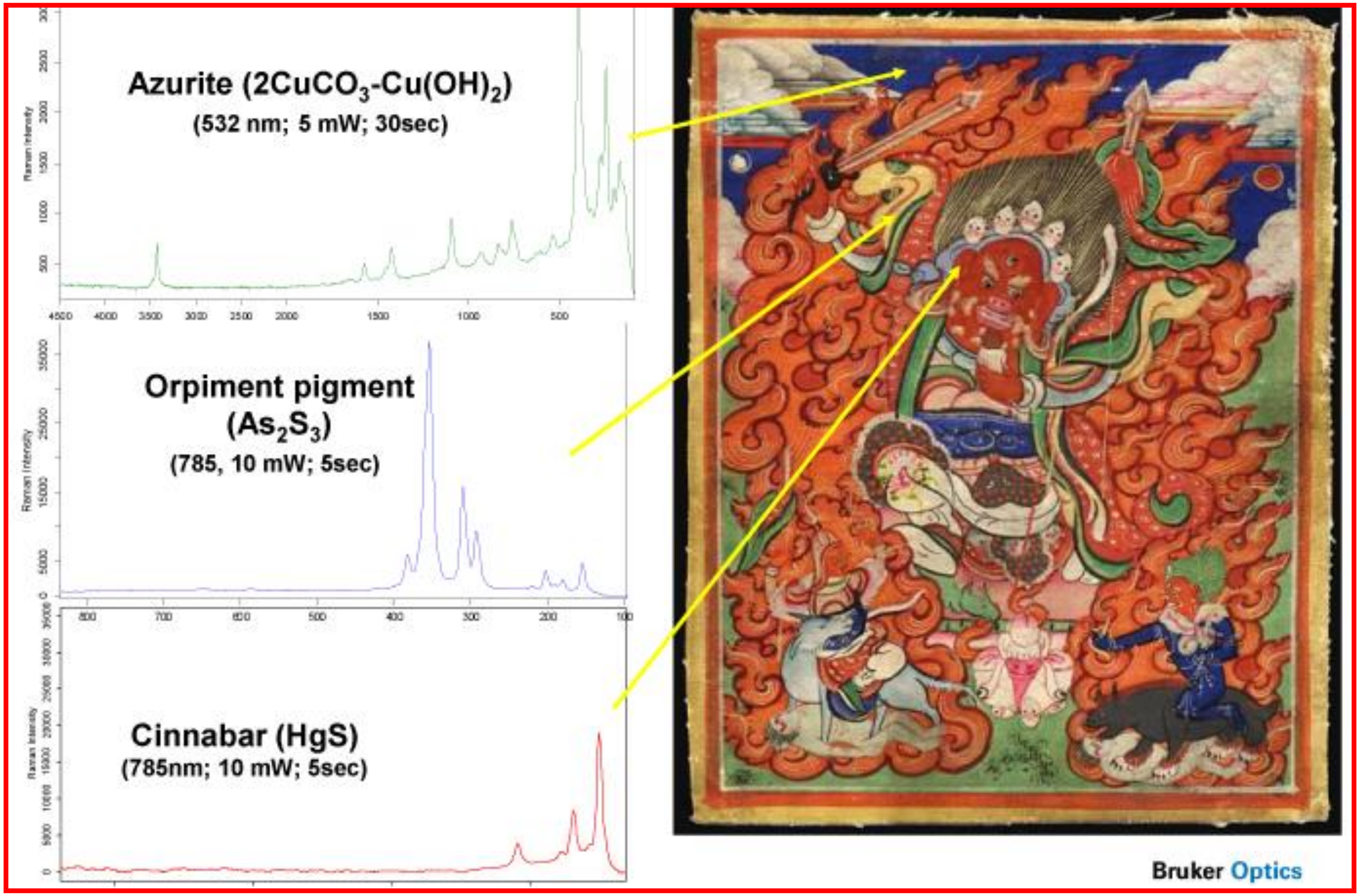


New IRUG Initiative:
Raman Spectral Database

Coming
Soon!

2009 IMLS National Leadership Grant
Advancing Digital Resources

Minerals / Pigments



Tibetan thangka from collection of Richard Ernst. Data courtesy of Tom Tague, Bruker Optics, Inc.

Synthetic Organic Colorants

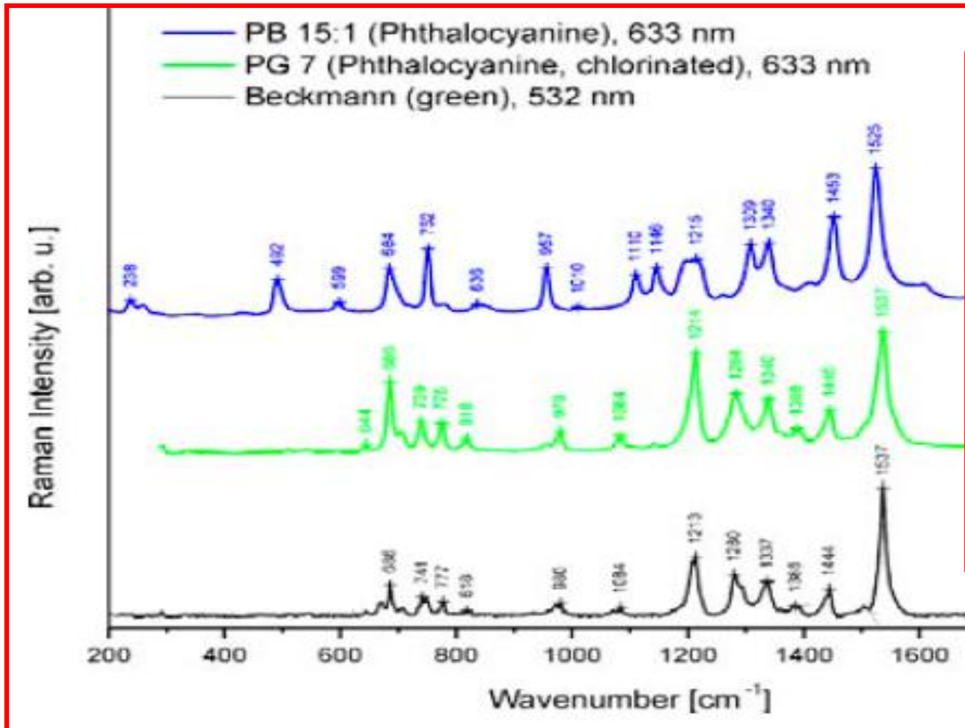


Figure 4: Spectra comparison of a green sample from "Woman with mandolin in yellow and red" (measured with laser 532 nm) with PG 7 (examined with laser 633 nm) and PB 15:1 (examined with laser 633 nm).

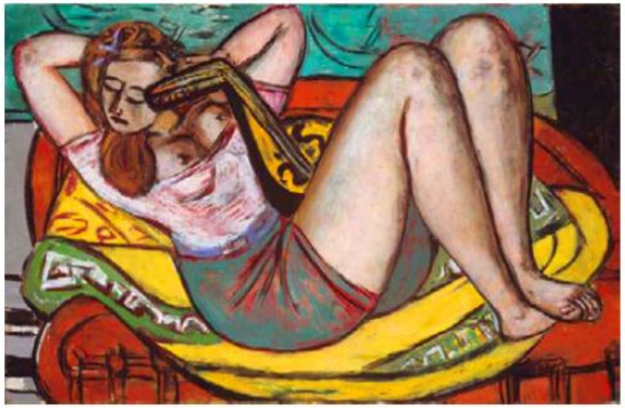
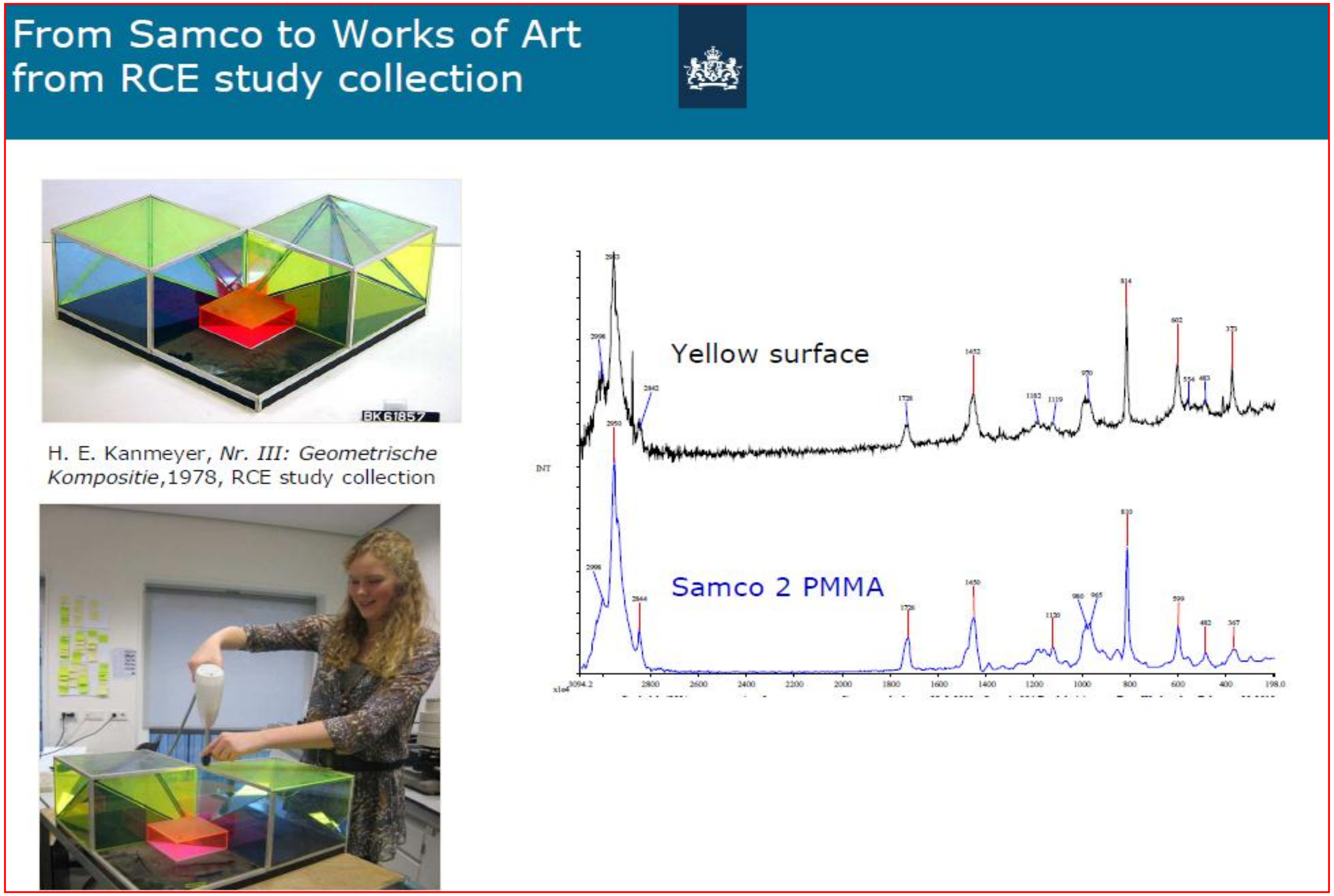


Figure 2: Max Beckmann, "Woman with mandolin in yellow and red", 1950, canvas, 92 x 140 cm, Bayerische Staatsgemäldesammlungen (Inv. No. 1532).

Lutzenberger, K. and Stege, H., "From Beckmann to Baselitz", IRUG 8, 2008

Polymers / Plastics



From Samco to Works of Art
from RCE study collection

H. E. Kanmeyer, *Nr. III: Geometrische Kompositie*,1978, RCE study collection

Suzan de Groot, Cultural Heritage Agency of the Netherlands, Amsterdam, NL

SERS

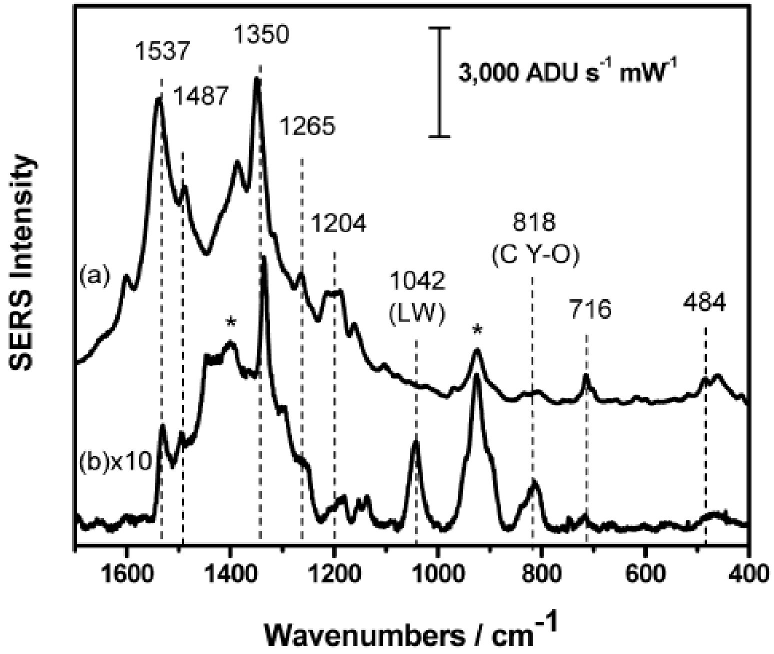


Figure 7. SER spectra of (a) pastel stick no. 7 and (b) sample no. 10 “fleshtone in face” from Mary Cassatt’s “Sketch of Margaret Sloane, Looking Right” (multiplied by 10 for ease of comparison). Peaks which are characteristic for the unidentified red pigment, which also appears in pastel stick no. 7, are labeled. Peaks due to lead white (LW) and chrome yellow-orange (C Y-O) are also labeled.

Figure 6. Mary Cassatt, pastel study: “Sketch of Margaret Sloane, Looking Right” (pastel on tan wove paper, measuring 410 mm × 330 mm; gift of Laura May Ripley, AIC 1992.158).

Brousseau et al., “SERS: A Direct Method to Identify Colorants in Various Artist Media”, *Analytical Chemistry*, 2009, 81, 7443-7447.

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman revealed: a short history of the technique in art and artifact studies

Greg Smith

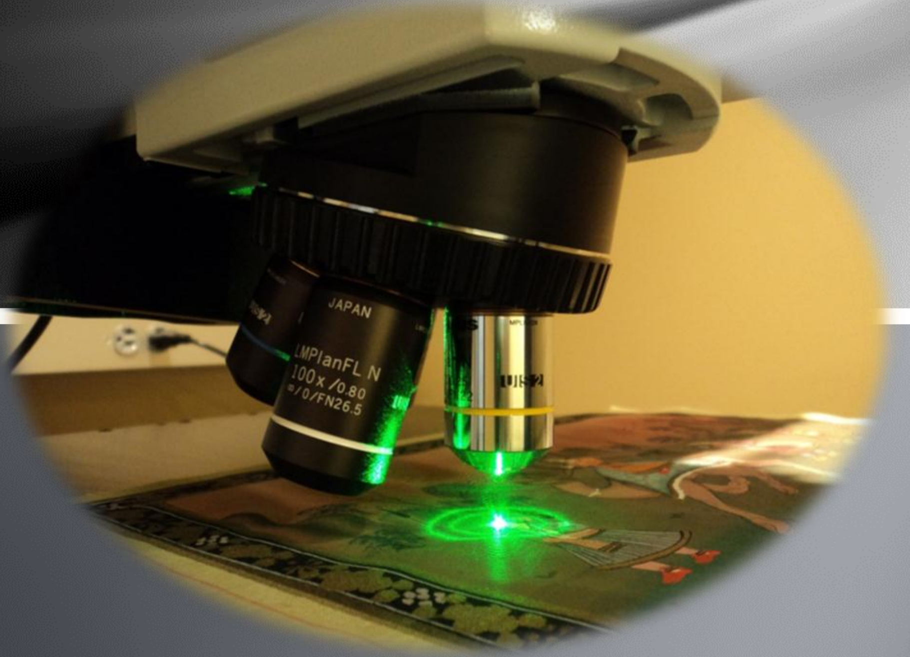
Indianapolis Museum of Art, US

THURSDAY, SEPTEMBER 27: LECTURE 1

Raman Reviewed

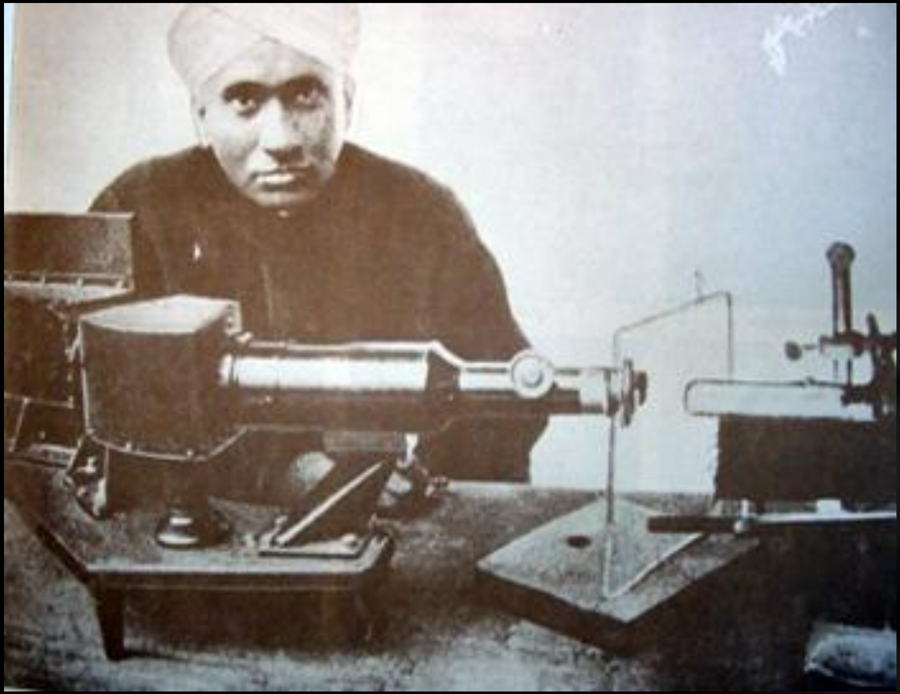
A Short History of the Technique in Art and Artifact Studies

Greg Smith



INDIANAPOLIS MUSEUM OF ART
IMA

C.V. Raman



- C.V. Raman observed inelastic scattering on Feb 28, 1928
- Reported results in *Nature*, March 31st, 1928
- Passed over for Nobel Prize in 1928 (Richardson) and 1929 (de Broglie)
- Awarded Nobel Prize in Physics in 1930

. . . we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state (Feb 16th, 1928).

Raman's Raman

- Raman & Krishnan (1928) *Nature*, 122, p. 619
- Liquid benzene excited by mercury arc at 435.8 nm & recorded on a photographic plate
- Arrows mark vibrational bands at 16.55, 11.78, 10.10, 8.51, 6.27, and 3.267 μ
- Even observed 16.55 and 10.10 μ anti-Stokes lines

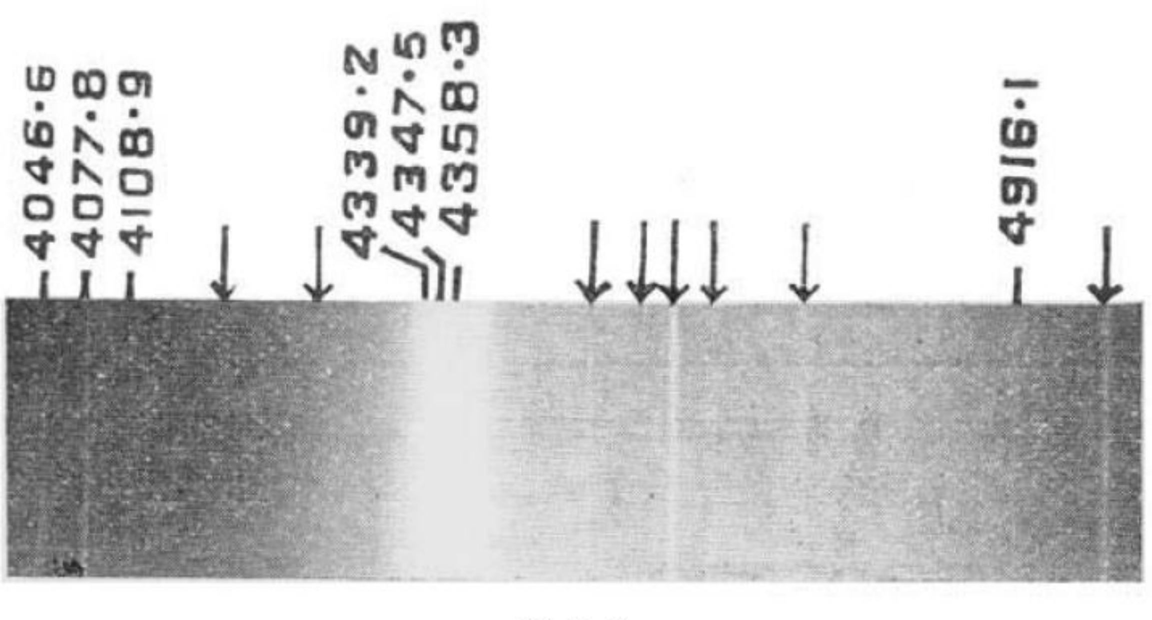


FIG. 1.

Controversial Discovery

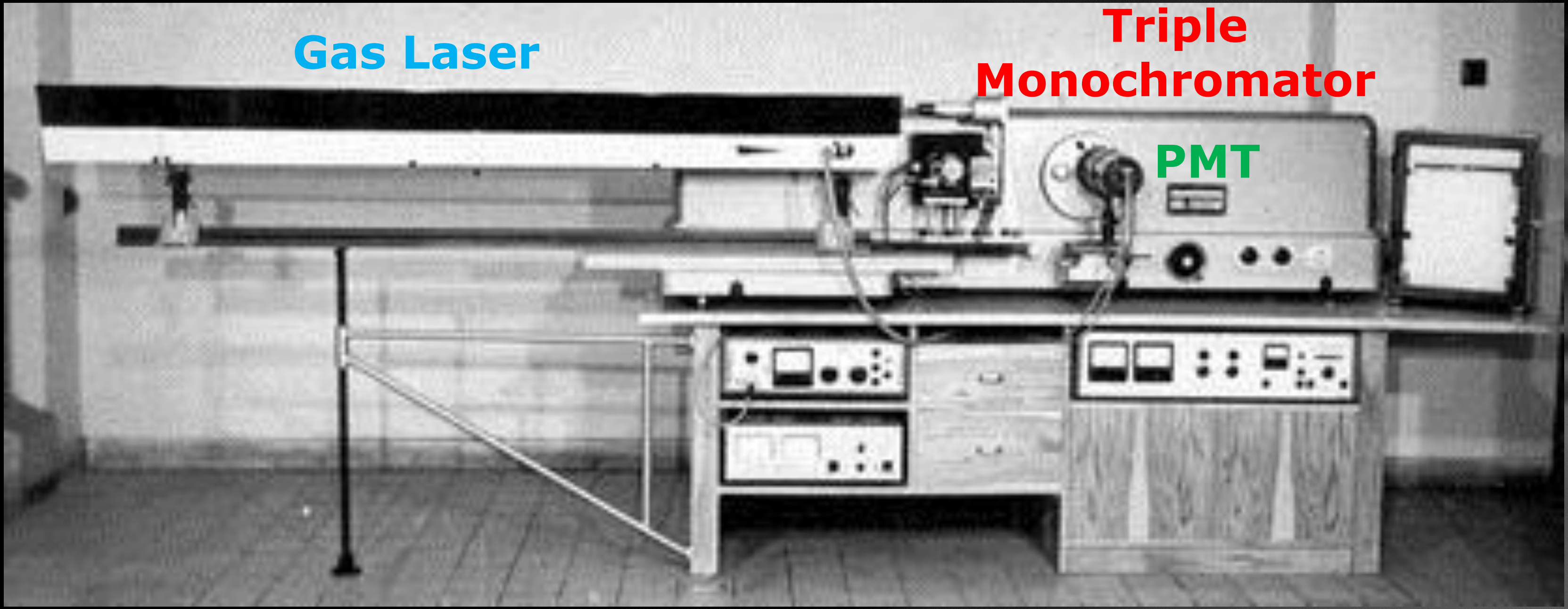
- Theoretical inelastic scattering was not a new idea by the time C. V. Raman observed it
- Leonid Mandelstam observed “Raman” scattering on Feb 21, 1928
- First reported his results on April 27, 1928
- Russians call the phenomenon “combinatorial scattering”

Advantages for Art/Artifacts

Raman spectra provide information on authenticity, provenance, ancient technology, trade patterns, artefact condition, and age

- molecular specificity
- non-destructive/in situ
- transportable/portable
- high spatial resolution
- application to large, irregular shaped objects
- sharp bands = relatively few band overlaps
- immune to atmosphere
- no sample preparation

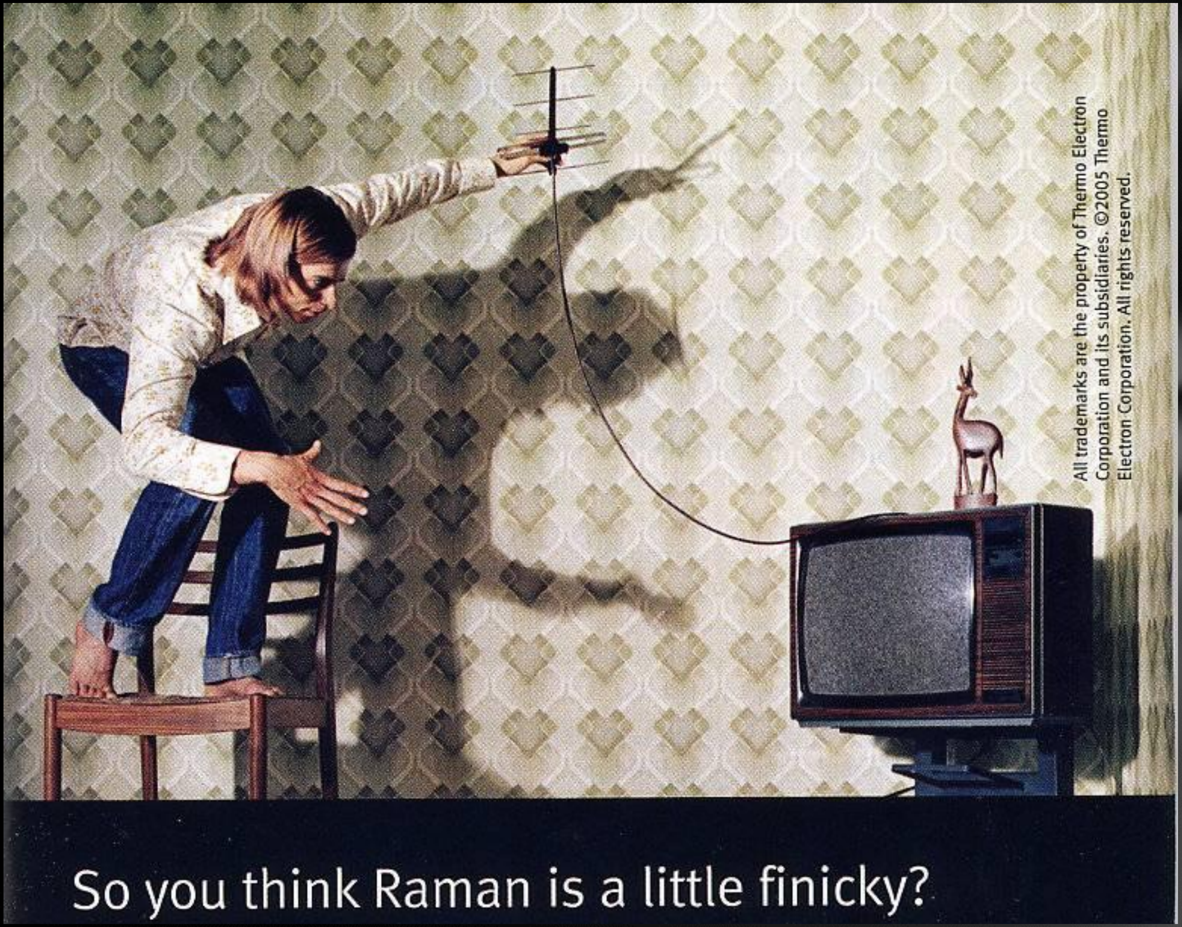
Early Instruments



"So far, indeed, there have been all but insuperable difficulties in the way of studying these ultrared oscillations, because that part of the spectrum lies so far away from the region where the photographic plate is sensitive. Raman's discovery has now overcome these difficulties . . ."

-from C. V. Raman's Nobel Award Commendation, 1930

A Finicky Experiment



The Raman experiment is generally more tedious and costly than IR spectroscopy, but chemists go to the trouble of collecting Raman data for many reasons. . .

-Shriver, Atkins, & Langford, 1994

The Raman effect is however a very weak one and good spectra are not easy to obtain. It seems unlikely to ever compete with FTIR and the infrared microscope.

- Mills & White, 1994

In the beginning . . .

- P. Dhamelincourt et al. (1979) “Laser Raman Molecular Microprobe” Analytical Chemistry, 51, A414.
- Couple microscope to Raman spectrometer and showed varied applications, including art analysis.

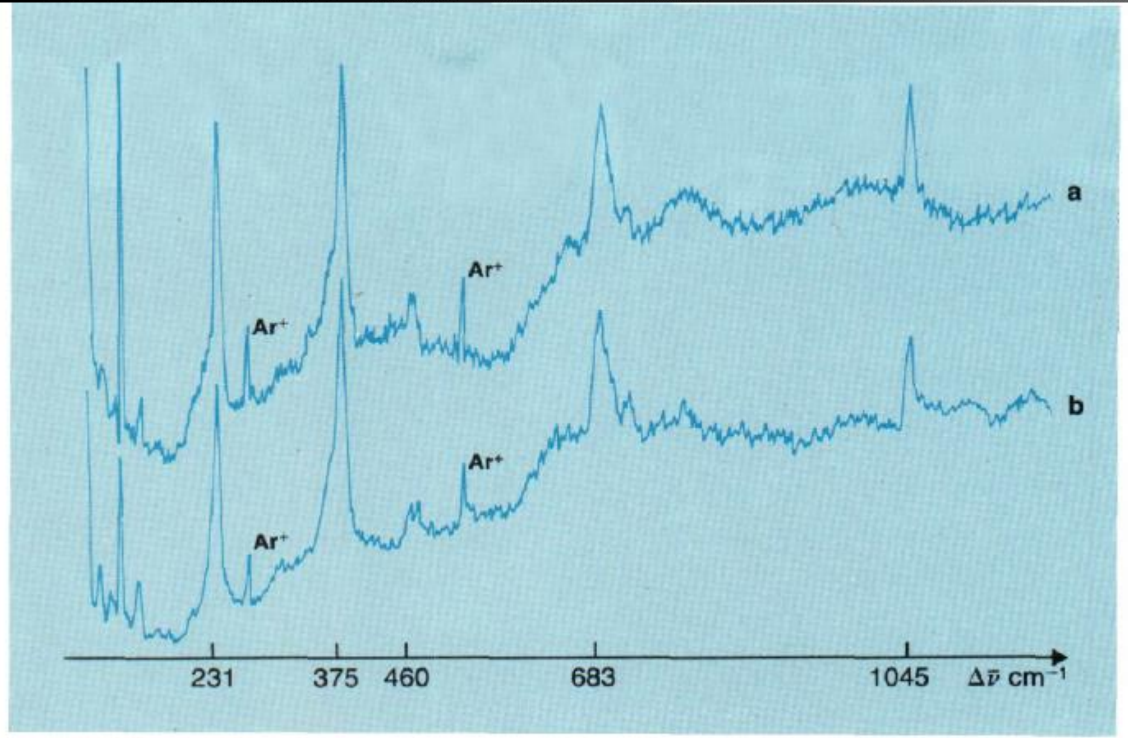
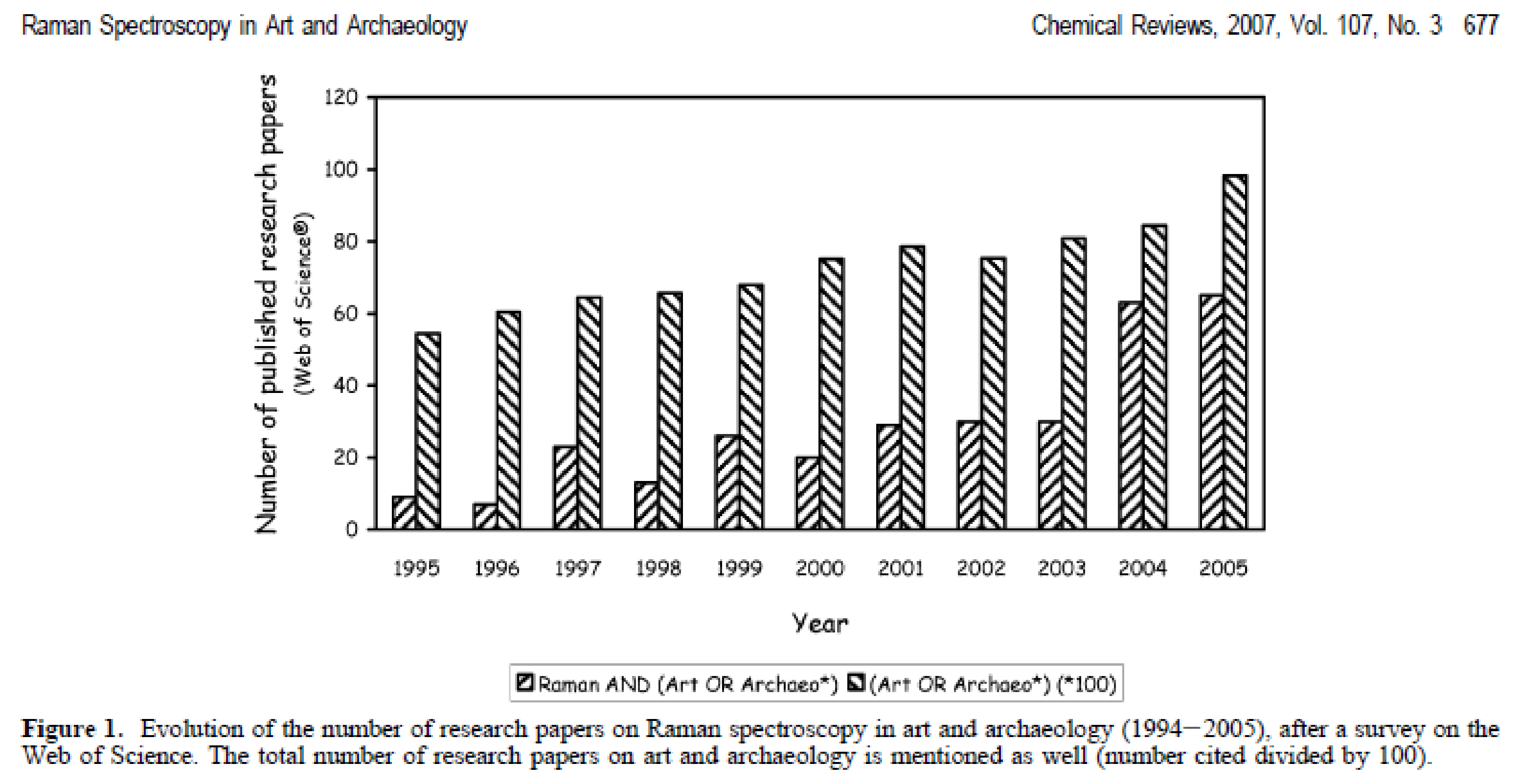


Figure 7. Raman spectra obtained from a) precious Chinese vase, b) specimen of serpentine

Publications



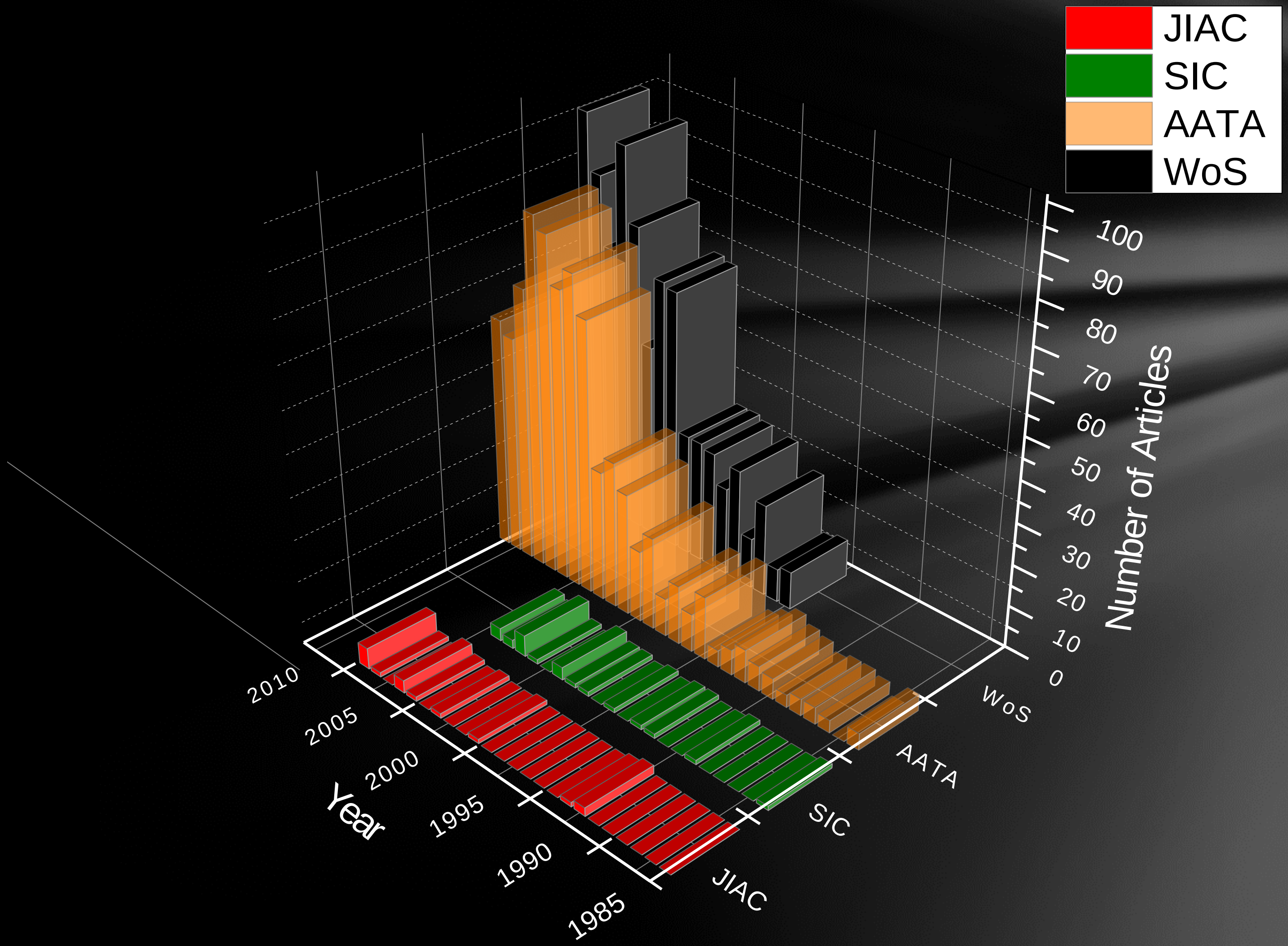
Raman Spectroscopy in Art and Archaeology

Chemical Reviews, 2007, Vol. 107, No. 3 677

Figure 1. Evolution of the number of research papers on Raman spectroscopy in art and archaeology (1994−2005), after a survey on the Web of Science. The total number of research papers on art and archaeology is mentioned as well (number cited divided by 100).

Vandenabeele et al., *Chemical Reviews*, **2007**, *107(3)*, 677.

Publications



Focused Meetings

Raman in Art and Archaeology (RAA)

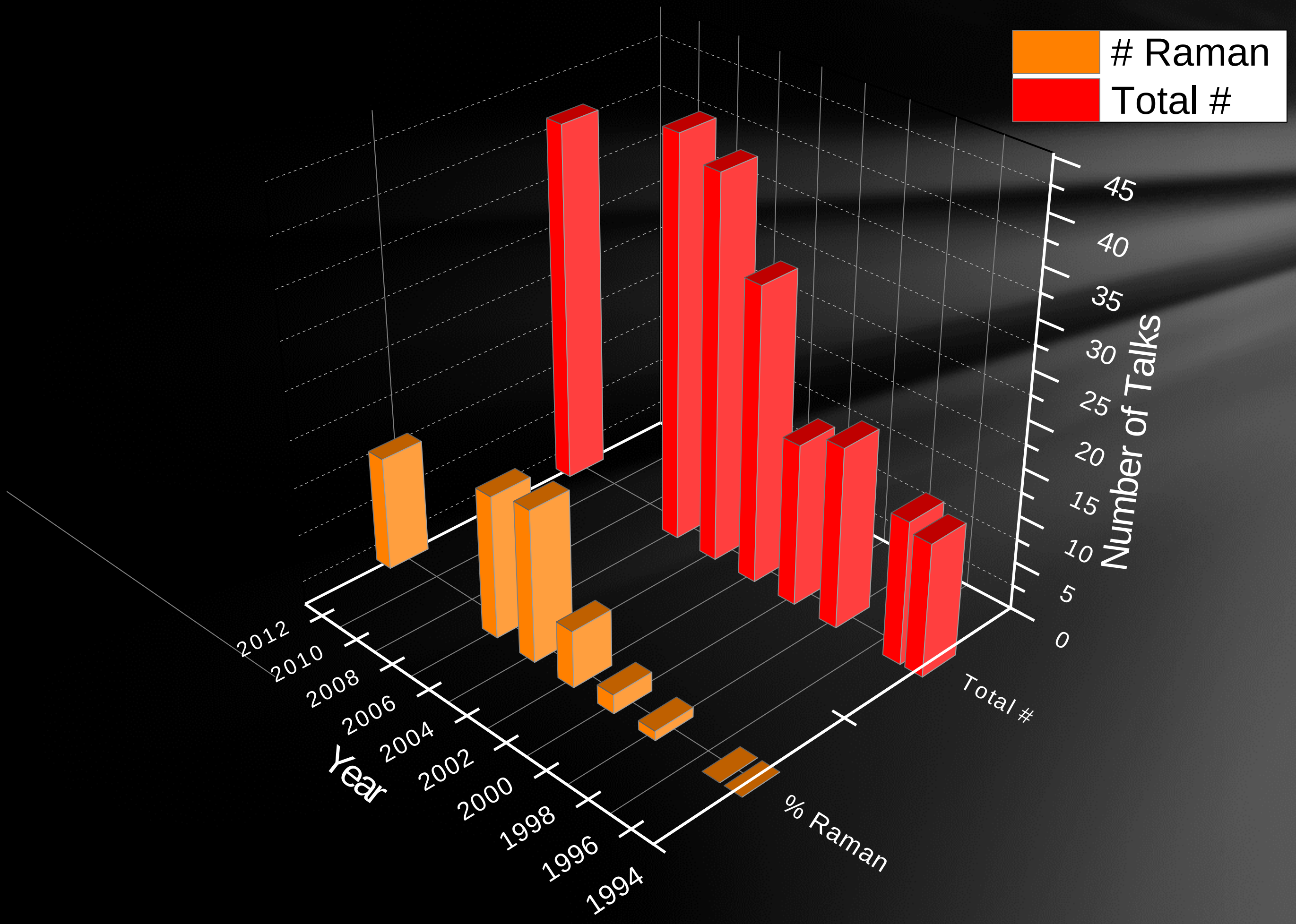
- 2001 London
- 2003 Ghent
- 2005 Paris
- 2007 Modena
- 2009 Bilbao
- 2011 Parma

6th International Congress on the Application of Raman Spectroscopy in Art and Archaeology

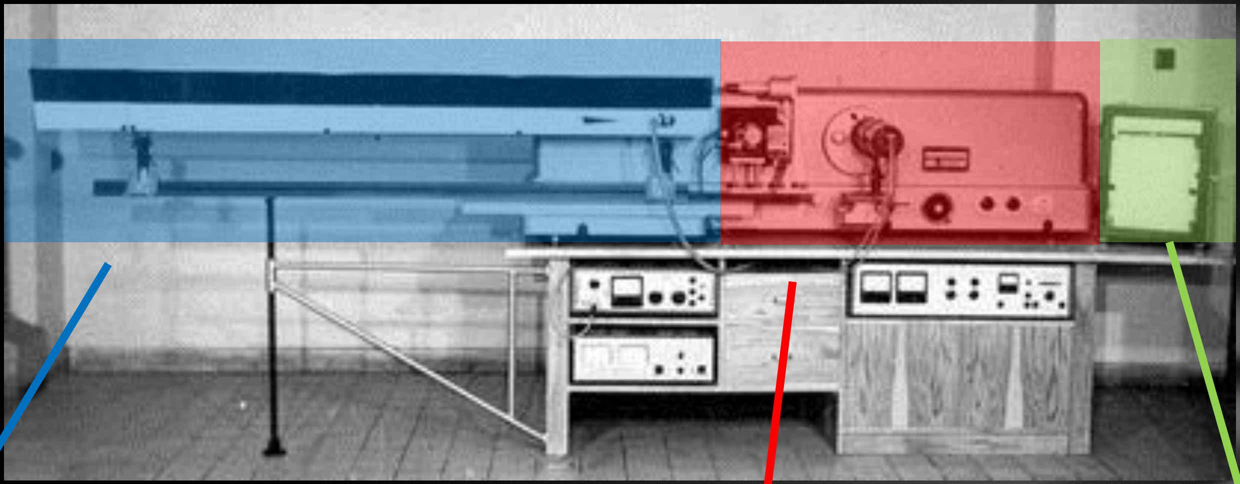
Parma, 5-8 September 2011

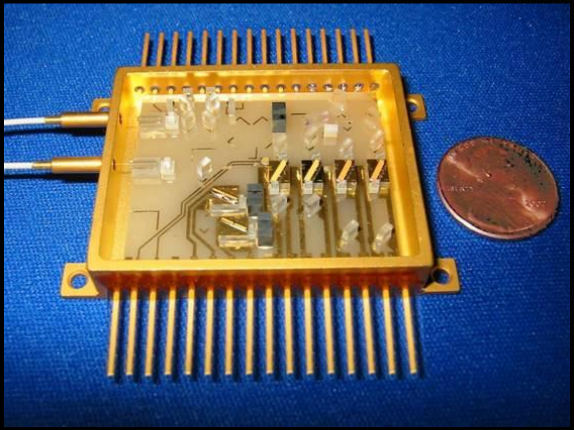
IRUG

- It’s always been “Infrared **and** Raman” although the Raman has featured more in the meetings than the database

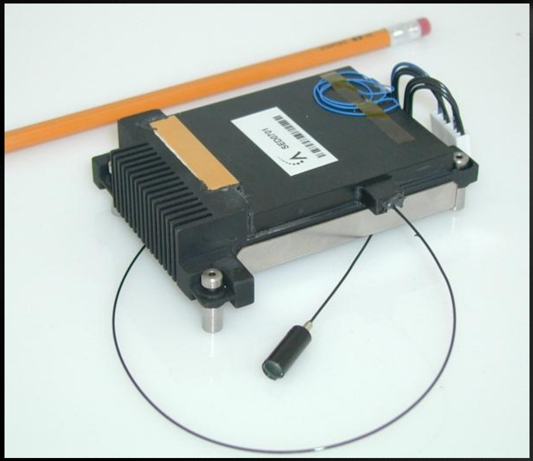


Faster, Better, & a little Cheaper





785 nm (NIR) cavity-stabilized cooled laser. 400mW output power, <1W consumed

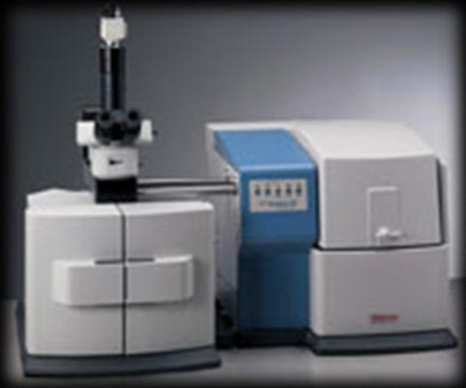


Single-dispersive 2048 channel cooled CCD spectrometer, holographic gratings, dielectric notch filters for Rayleigh/stray-light rejection.

Fast, inexpensive, high power computing

Manufacturers

Dispersive



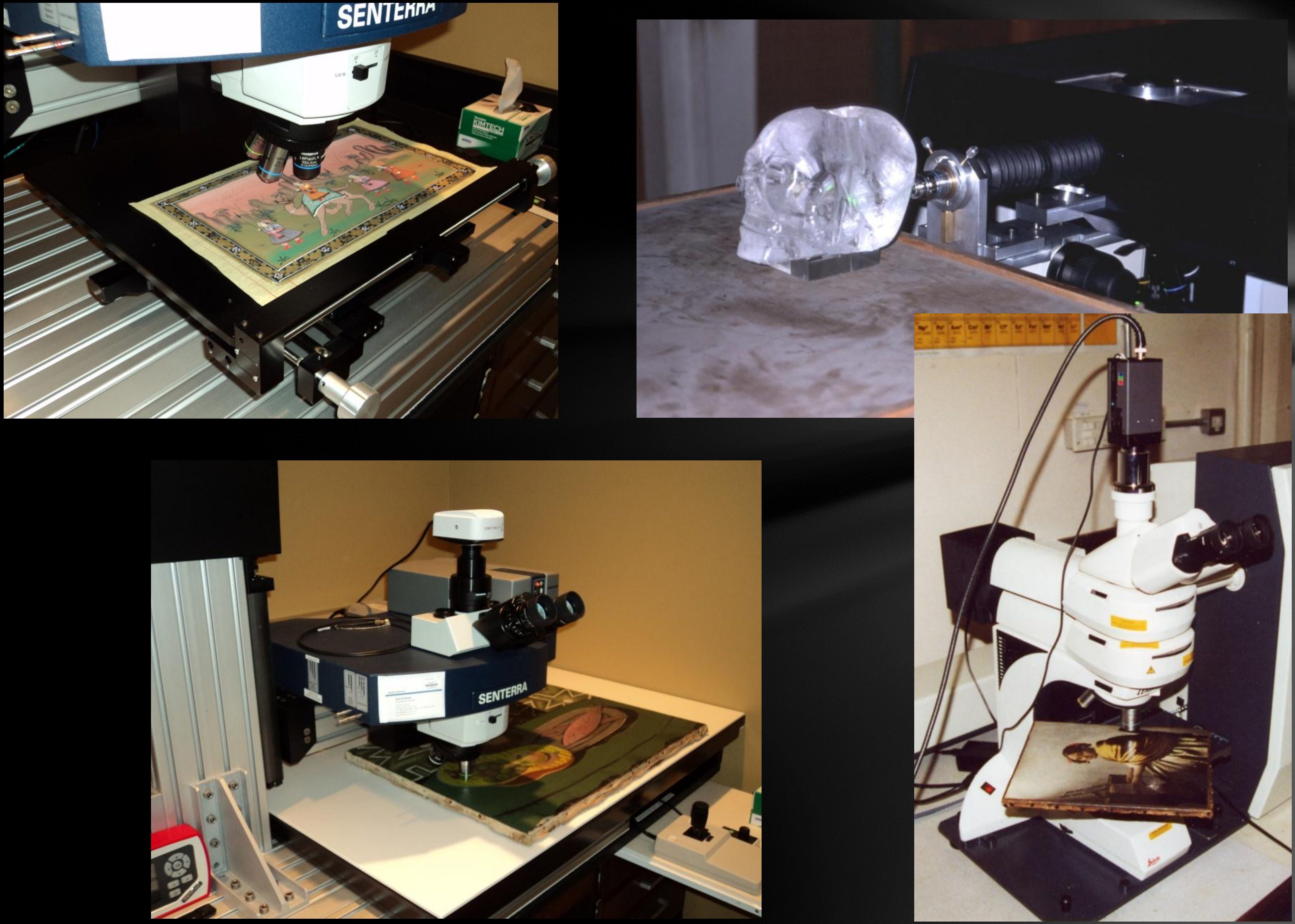
FT-Raman

Handheld

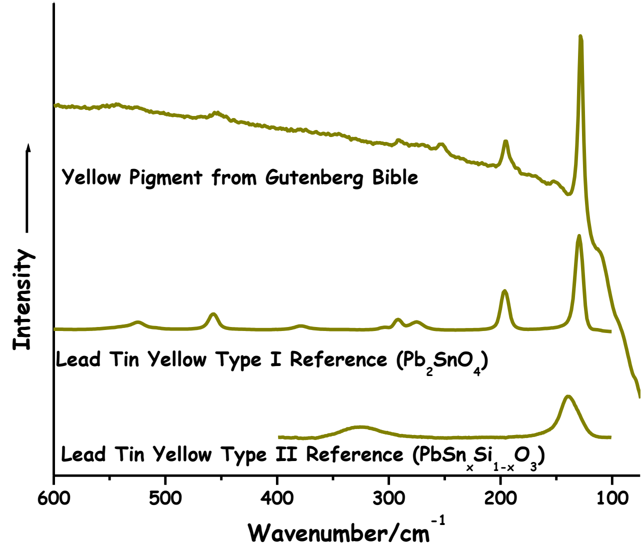
- Renishaw – RM1000, inVia (AFM-Raman, SEM-Raman, FTIR-Raman)
- Thermo Scientific – DXR, Almega, NXR, FirstDefender, TruScan
- Horiba – Dilor, LabRam, ARAMIS, XploRA
- Bruker – Senterra, RamanScope III, RAM II, MultiRAM

- DeltaNu – ExamineR, Inspector, ReportR, RockHound
- Ocean Optics – PeekSeeker, Pinpointer
- WiTec – Alpha
- BaySpec – Nomadic, FirstGuard

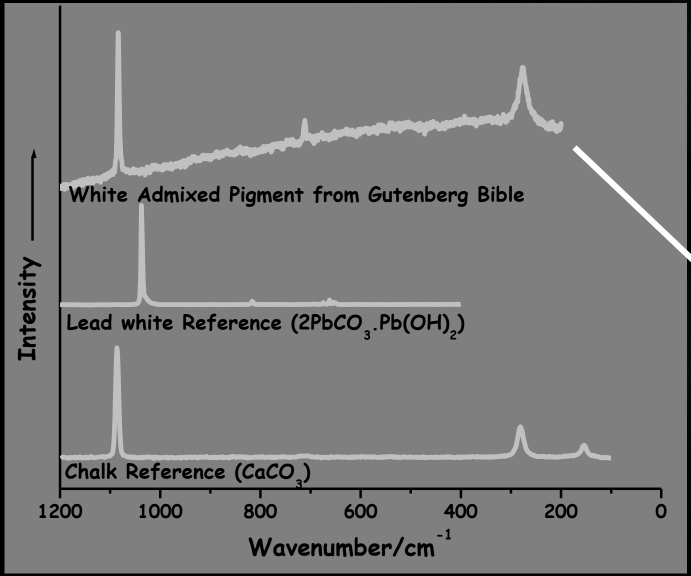
Flexible Sampling



Fiber Optics



In situ microscope

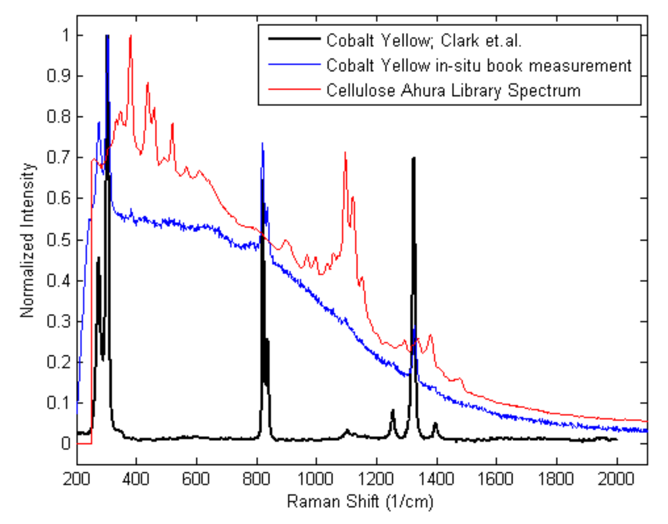


In situ probe attachment

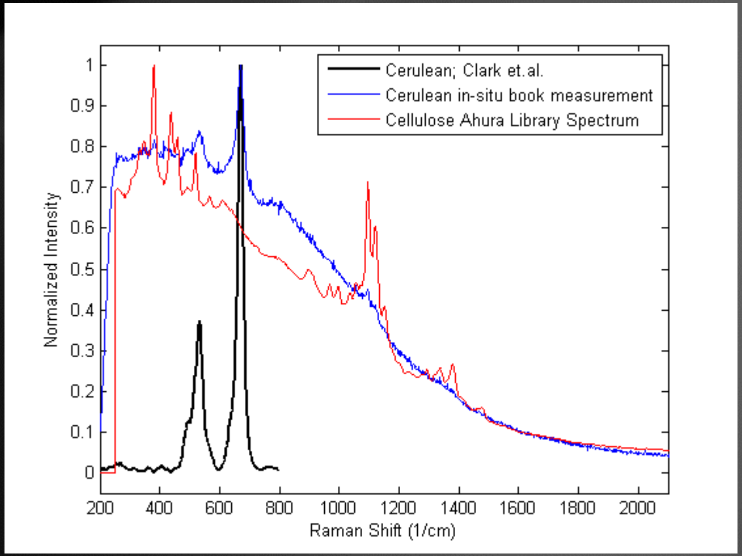
Portable Instruments

- Single laser
- Magnification/focus
- Laser power control
- Stability/positioning

Auroelin (cobalt yellow)

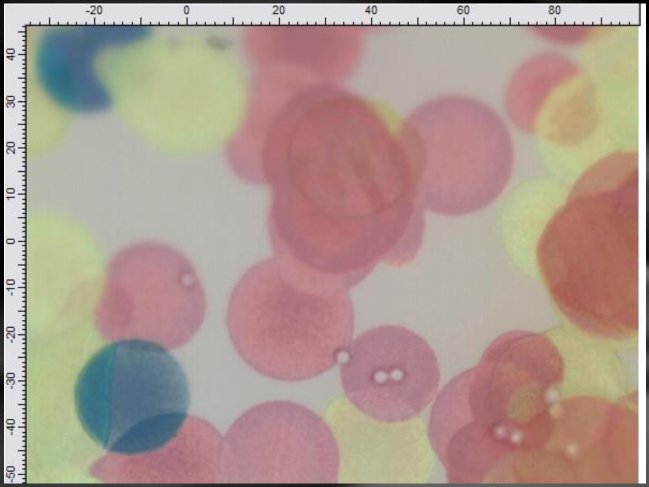


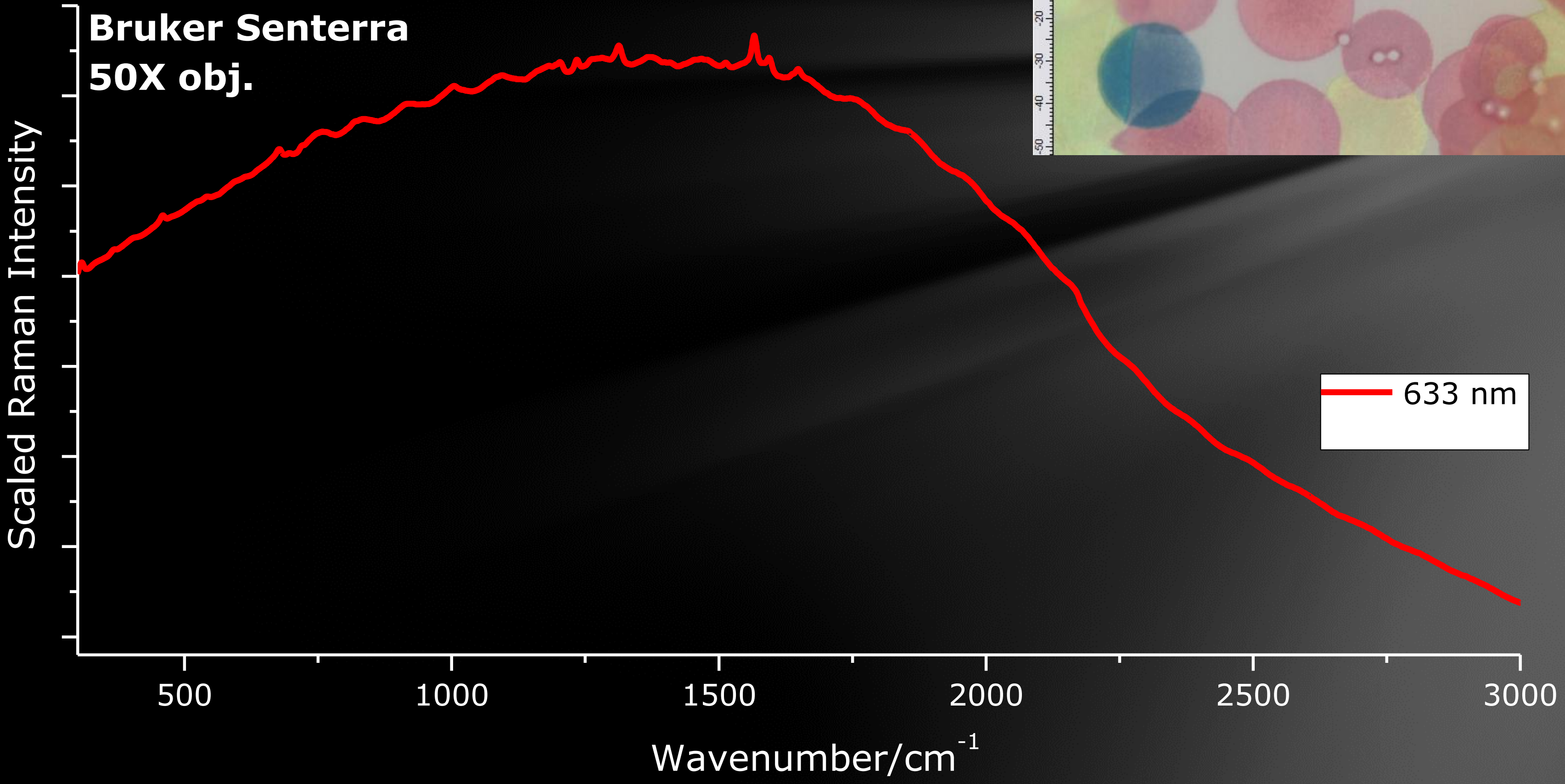
Cerulean blue



Fluorescence

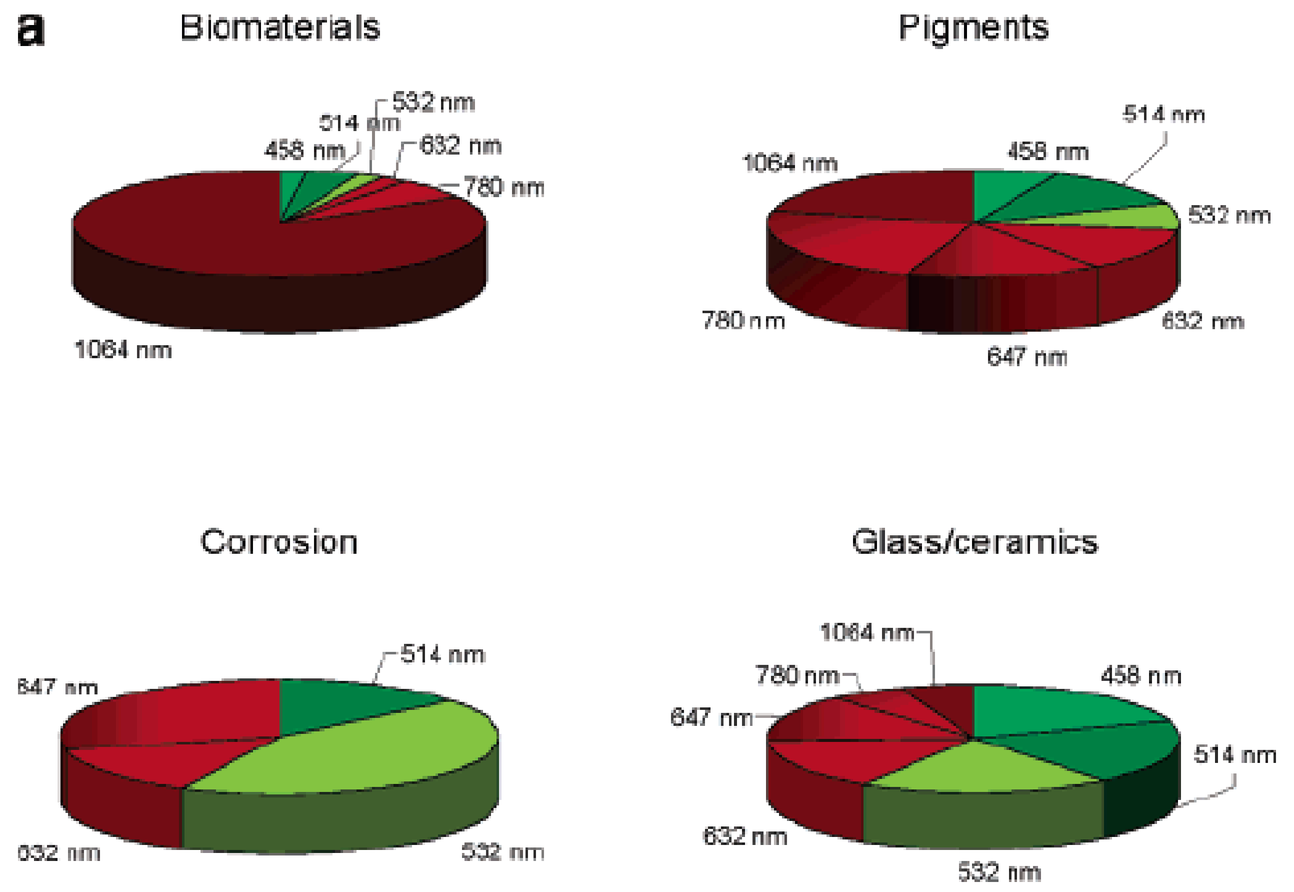
- Common fluorescence background from the red dye cloud in an inkjet photographic print





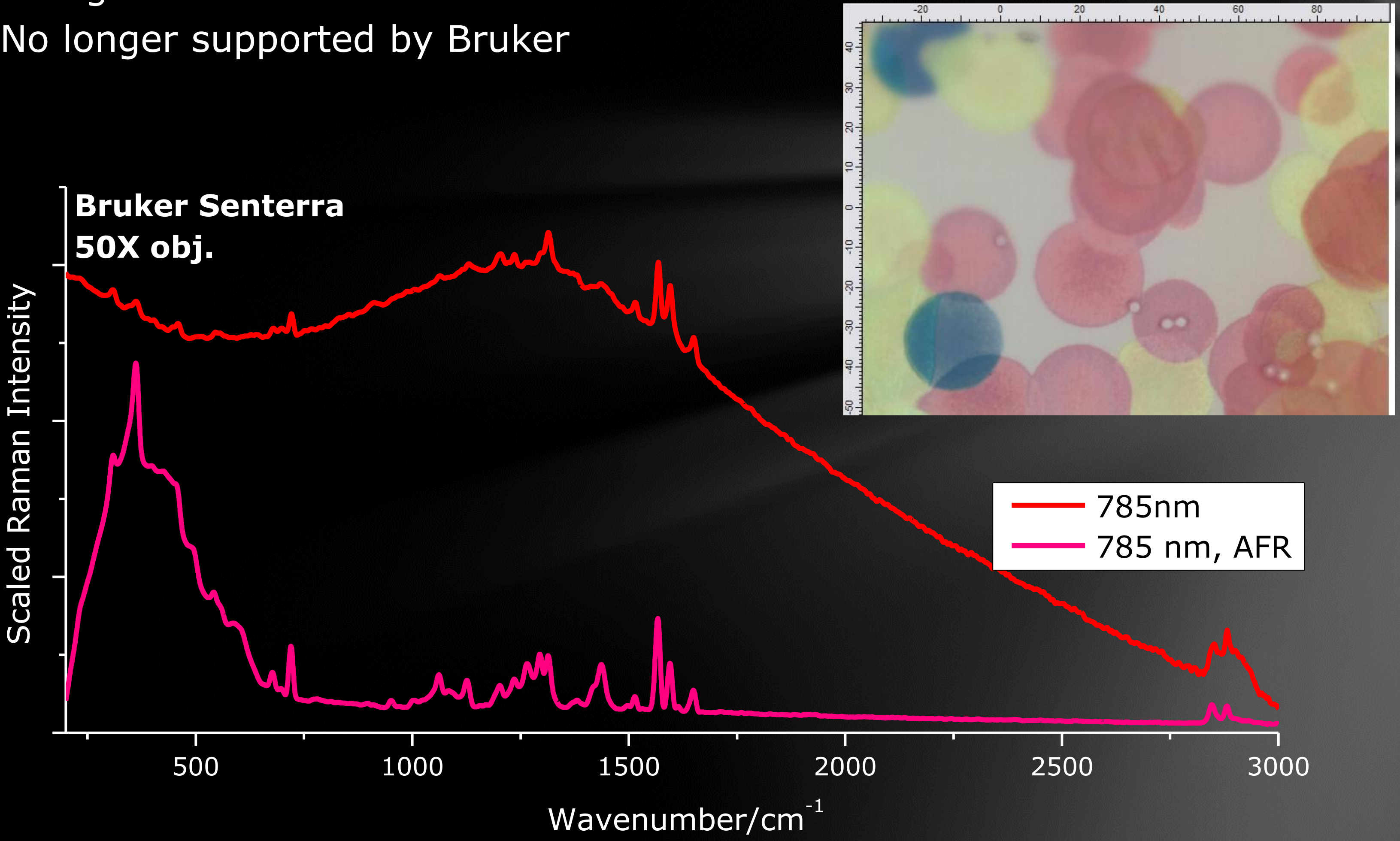
Lasers

- Use of long wavelength lasers (dispersive and FT-Raman) avoids fluorescence in organic media
- Solid state lasers appear at 785nm in 1998 and 532nm in 2001



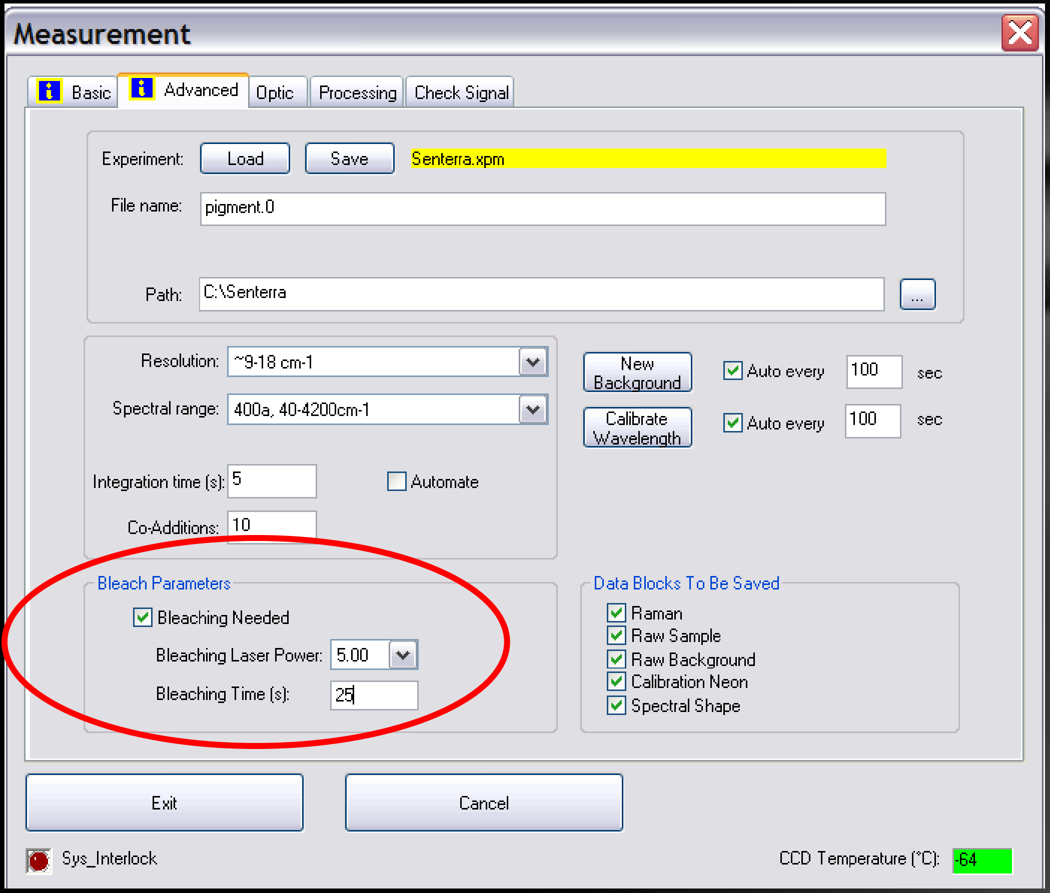
Fluorescence Rejection

- SERDS (**S**hifted **E**xcitation **R**aman **D**ifference **S**pectroscopy) or AFR (**A**utomatic **F**luorescence **R**ejection) occasionally overcomes fluorescence background
- No longer supported by Bruker



Photobleaching

- Automated option on many instrument companies' software
- Often not desirable or effective for artworks



Measurement

Experiment: Senterra.xpm

File name: pigment.0

Path: C:\Senterra

Resolution: ~9-18 cm-1

Spectral range: 400a, 40-4200cm-1

☑ Auto every 100 sec

☑ Auto every 100 sec

Integration time (s): 5

☐ Automate

Co-Additions: 10

Bleach Parameters

☑ Bleaching Needed

Bleaching Laser Power: 5.00

Bleaching Time (s): 25

Data Blocks To Be Saved

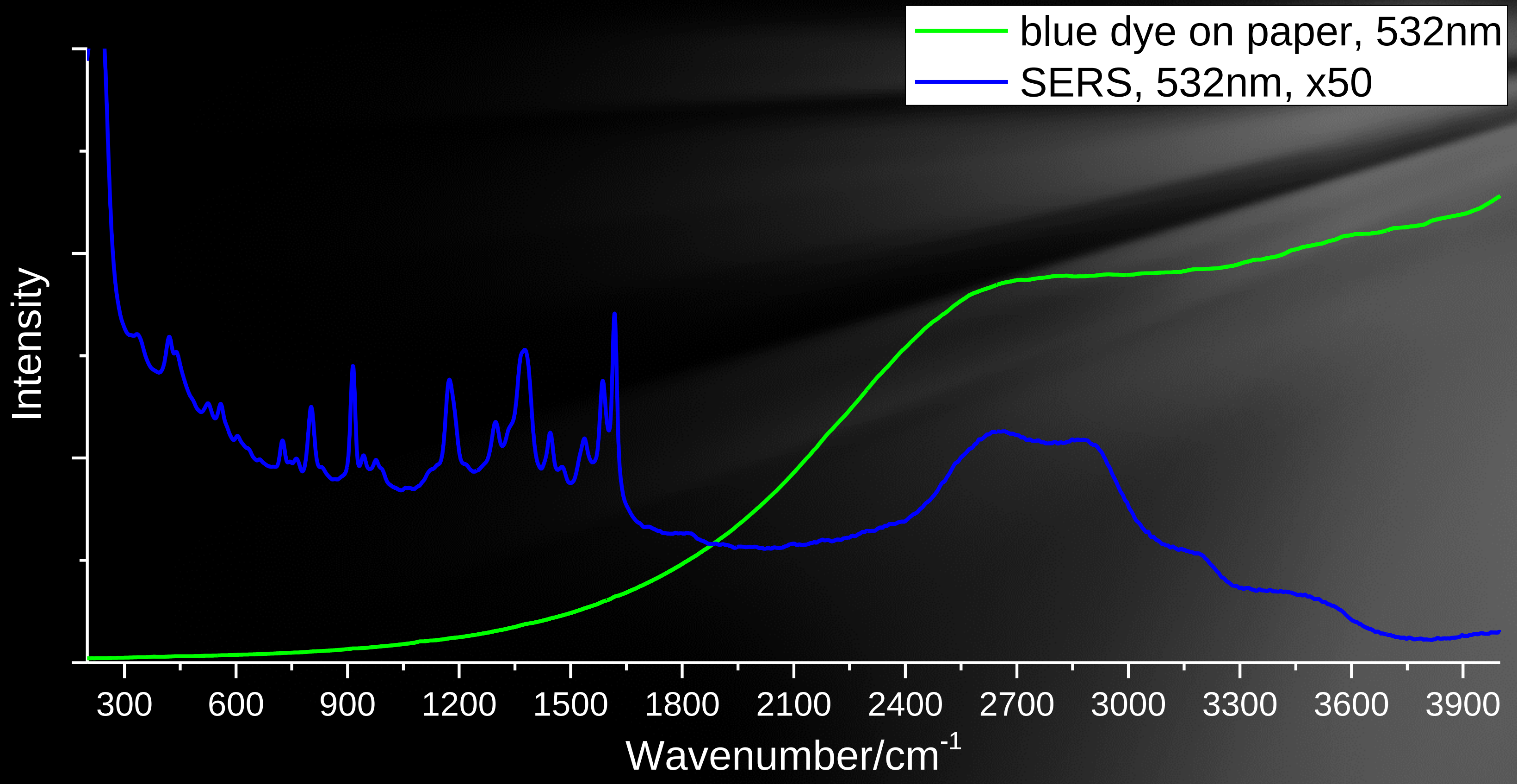
☑ Raman
☑ Raw Sample
☑ Raw Background
☑ Calibration Neon
☑ Spectral Shape

Sys_Interlock

CCD Temperature (°C): -64

SERS

- **S**urface-**E**nhanced **R**aman **S**pectroscopy uses electromagnetic coupling to roughened metal surfaces to magnify the Raman signal
- SERS spectra can be different from normal Raman spectra, necessitating new spectral libraries for SERS experiments



Online Databases

- UCL Pigment Database (http://www.chem.ucl.ac.uk/resources/raman/index.html)
- RRUFF (http://rruff.info/)
- Lyon (http://www.ens-lyon.fr/LST/Raman/)
- RASMIN (http://riodb.ibase.aist.go.jp/rasmin/E_index.htm)
- Romanian Database of Raman Spectroscopy (http://rdrs.uaic.ro/)
- Siena (http://www.dst.unisi.it/geofluids-lab/Raman%20intro.htm)
- Parma (http://www.fis.unipr.it/phevix/ramandb.php)
- E-VISART (http://www.ehu.es/udps/database/database.html)
- IRUG (www.IRUG.org)

“. . . quality of spectra somewhere between average and disastrous”

Raman Reviews

- Smith, G. D.; Clark, R. J. H. "Raman Microscopy in Art History and Conservation Science." *Reviews in Conservation*, **2001**, *2*, 92-106.
- Smith, G. D.; Clark, R. J. H. "Raman Microscopy in Archaeological Science." *Journal of Archaeological Science,* **2004**, *31*, 1137-1160.
- Vandenabeele, P.; Edwards, H. G. M.; Moens, L. "A Decade of Raman Spectroscopy in Art and Archaeology" *Chemical Reviews*, **2007**, *107*, 675-686.
- Clark, R. J. H. "Raman Microscopy as a Structural, Analytical and Forensic Tool in Art and Archaeology." *Chemistry in New Zealand*, **2011**, 13-20.
- Clark, M. P. A.; Clark, R. J. H. "Rutherford and Raman – Nobel Laureates Who Had Difficult Early Journeys to Success." *Journal of Raman Spectroscopy*, **2011**, *42*, 2173-2178.
- Das, R.S.; Agrawal, Y. K. "Raman Spectroscopy: Recent Advancements, Techniques and Applications." *Vibrational Spectroscopy*, **2011**, *57*, 163-176.
- Colomban, P. "The On-site/Remote Raman Analysis with Mobile Instruments: A Review of Drawbacks and Success in Cultural Heritage Studies and Other Associated Fields." *Journal of Raman Spectroscopy*, **2012**, in press.

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Basic principles of Raman spectroscopy

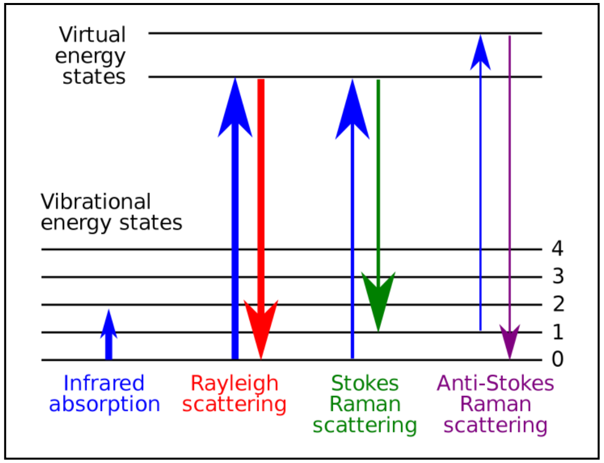
Jennifer Mass

Winterthur Museum, Garden and Library, US

THURSDAY, SEPTEMBER 27: LECTURE 2

Basic Principles of Raman Spectroscopy

Jennifer Mass
Winterthur Museum, Garden and Library, DE, US



Basic Principles of Raman Spectroscopy

Outline

What is Raman spectroscopy?

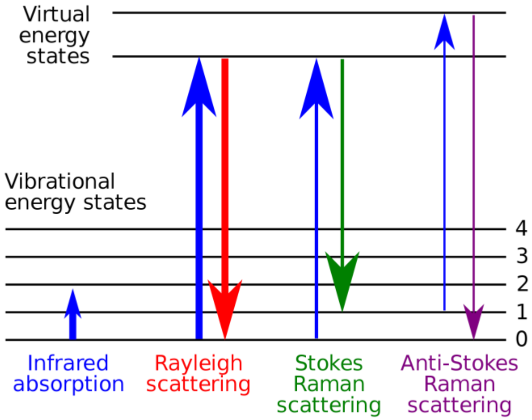
What can Raman do for me?

Information obtainable

How does it work?

Basic principles

Theory behind the technique



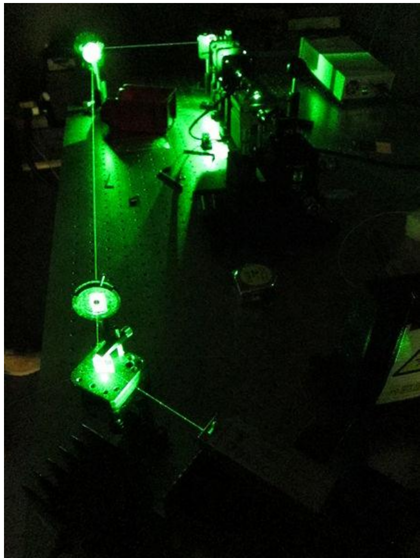
Why do I have to learn this?

Applications to art conservation

Practical Considerations:

Advantages/limitations

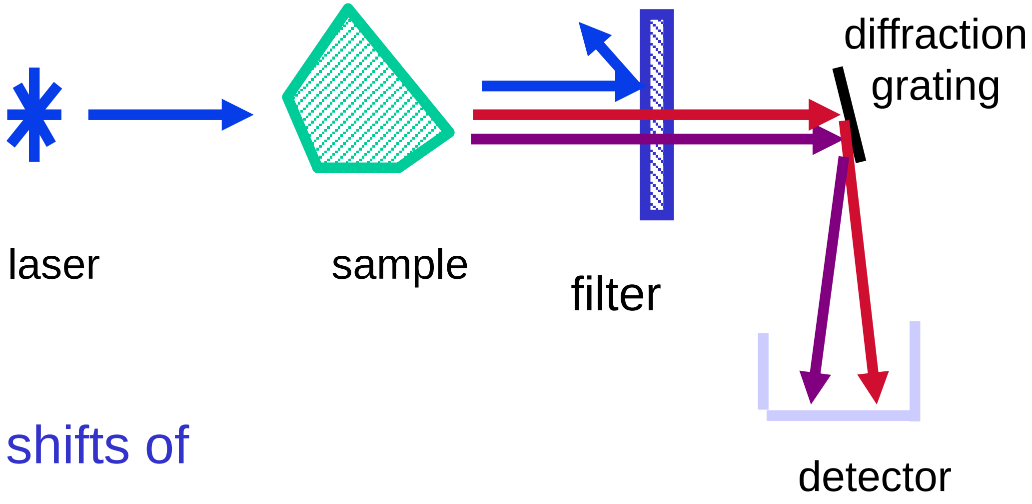
Standards, sample preparation



Basic Principles of Raman Spectroscopy

What is Raman spectroscopy?

- Vibrational spectroscopy
- Laser light scattering
- Compound identification
  - Even polymorphs
- Measure fingerprint of frequency shifts of the inelastically scattered light



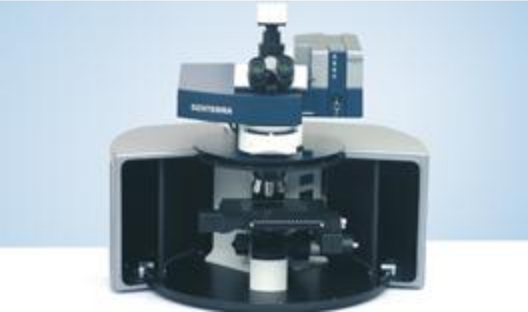
laser

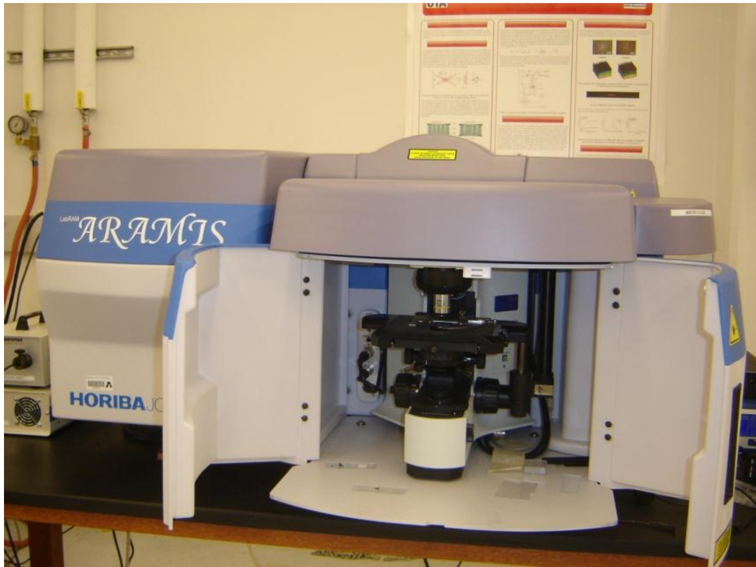
sample

filter

diffraction grating

detector





Basic Principles of Raman Spectroscopy

Why do we need another vibrational spectroscopy technique?

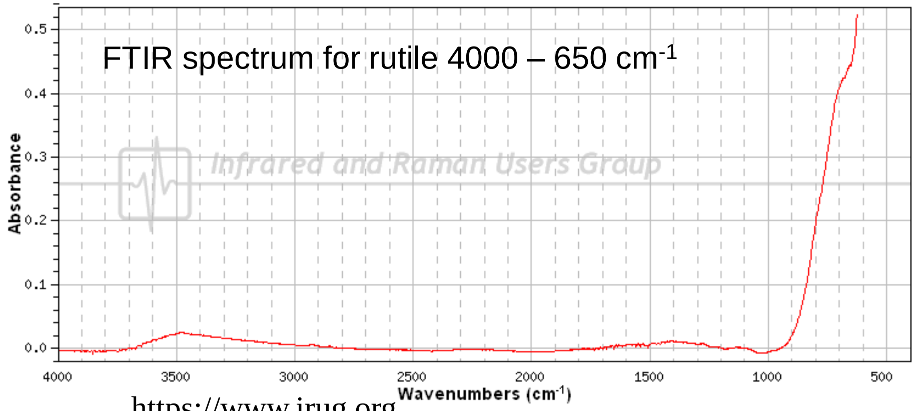
Molecular identification based on vibrational energy levels

FTIR (microscope/MCTA)

- 650 cm^{-1} – 4000 cm^{-1}
- Polyoxoanion pigments, corrosion products (carbonates, sulfates, chromates)
- Rutile spectrum (TiO_2) IRUG

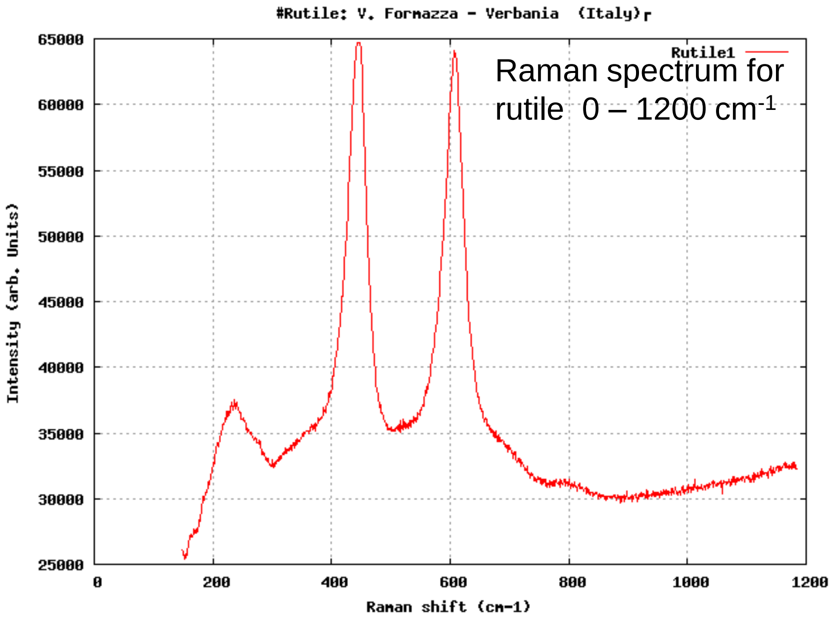
Raman

- Spectral range
- 100 cm^{-1} – 4000 cm^{-1}
- Oxides and sulfides
- HgS, Pb_3O_4, CuO, Cu_2O



FTIR spectrum for rutile 4000 – 650 cm^{-1}

https://www.irug.org



Raman spectrum for rutile 0 – 1200 cm^{-1}

https://www.fis.unipr.it/phevix/ramandb

Basic Principles of Raman Spectroscopy

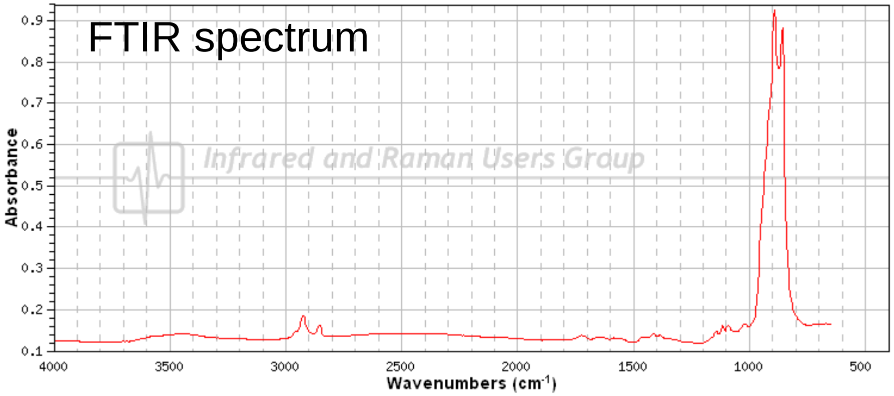
How does Raman Spectroscopy Differ from FTIR?

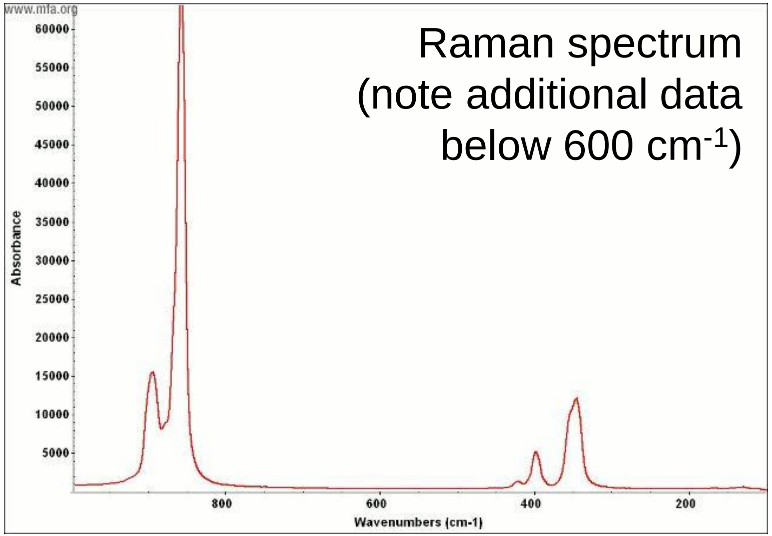
- **Raman scattering spectra & infrared absorption spectra**
- **Similar λ (ν) ranges**
  - **X axis in cm^{-1} (wavenumbers)**
  - **Y axis in intensity**

HOWEVER

- Functional groups & molecules that are IR active ≠ those that are Raman active
  - Techniques are complementary

Barium yellow $BaCrO_4$


FTIR spectrum


Raman spectrum (note additional data below 600 cm^{-1})

www.irug.org www.mfa.org/%5Fcameo/frontend/home.asp

Basic Principles of Raman Spectroscopy

- 1928 Indian physicist C. V. Raman
- Notices shifts in scattered light wavelengths depend on molecular structure
- 1930 Nobel prize in physics
- Raman's system: filtered sunlight, prism spectroscope, visual observation
- Major experimental challenge

Sir Chandrasekhara Venkata Raman, FRS

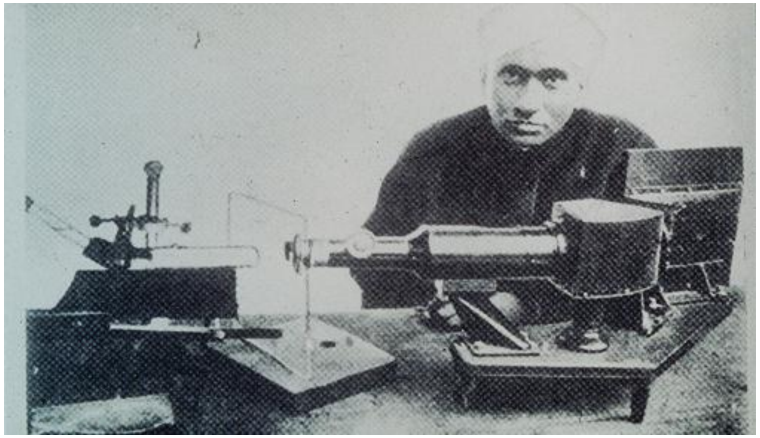
Raman effect –

- scattered light has shifted ν from incident light
- due to interaction with molecular vibrations

Basic Principles of Raman Spectroscopy

The Challenge to Collect Raman Spectra:

- To detect a signal weaker than the excitation signal by 6 – 8 orders of magnitude
  - Only tiny fraction of scattered light contains molecular information
  - Information in form of frequency shift
  - Almost all light scattering is Rayleigh scattering $\lambda_i = \lambda_s$



Huge experimental challenge

Basic Principles of Raman Spectroscopy

Why is this so?

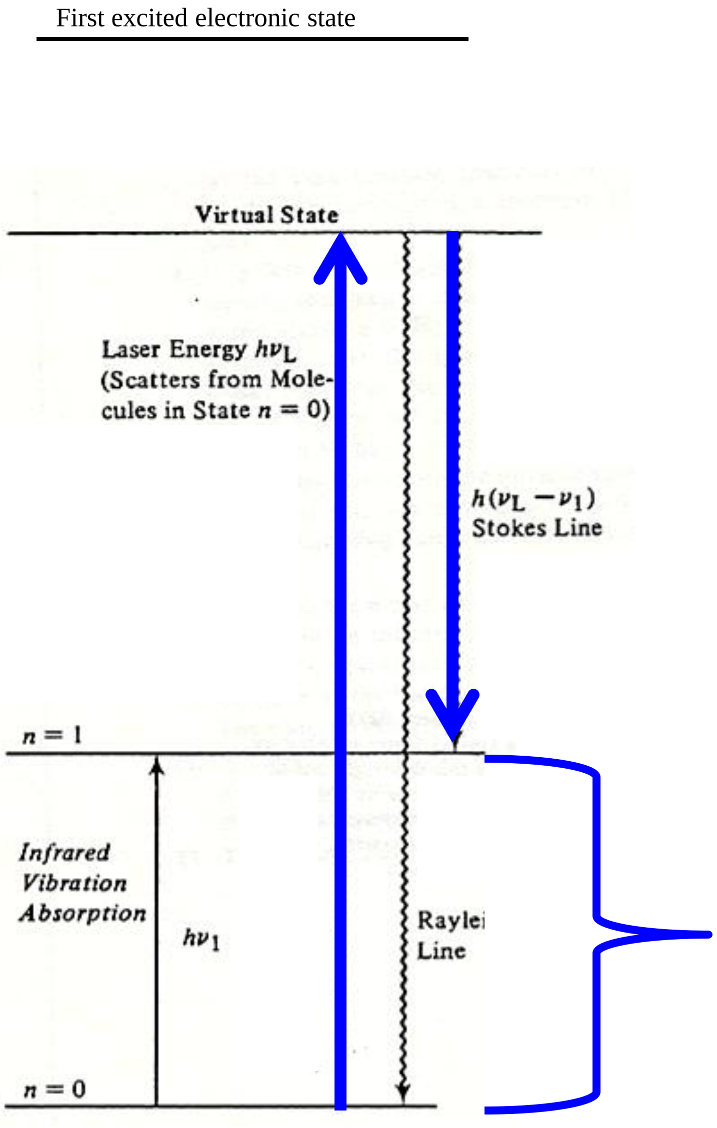
How does Raman Differ from FTIR?

FTIR

- Characteristic bands due to absorption IR
  - Frequency of incident EMR matches frequency of one of the molecule’s normal modes of vibration
  - Leads to an absorption
- Allow for molecular characterization or identification
- **Transition from vibrational ground state to 1 vibrational excited state**

Raman

- UV, VIS, or NIR light scattered from sample
- **Transition from electronic ground state and vibrational ground state (usually) to virtual excited electronic state**
- Return to different vibrational state in electronic ground state



Basic Principles of Raman Spectroscopy

What Can Raman Do for Me?

Phase ID/
fingerprinting

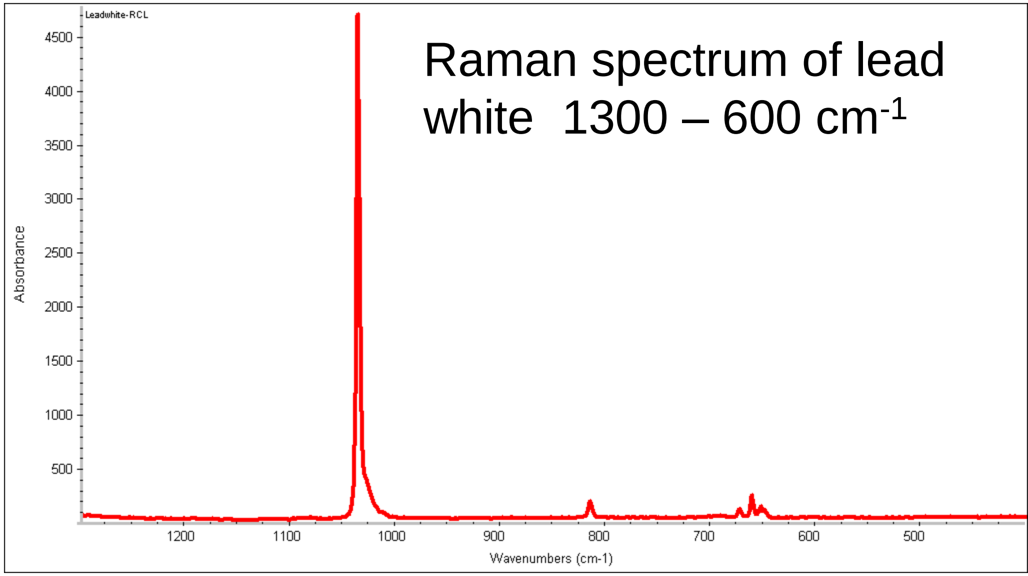
- pink watercolor

Pb present

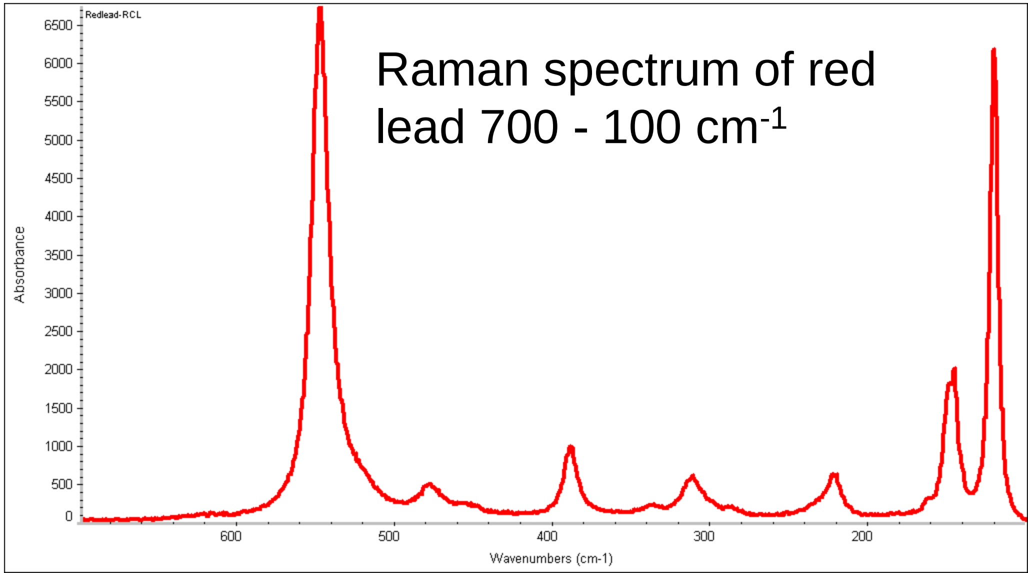
Pb_3O_4 vs. $2PbCO_3.Pb(OH)_2$

XRD, FTIR, Raman,
Compound/phase ID

Perform after elemental analysis
XRF, SEM-EDS



Raman spectrum of lead white 1300 – 600 cm^{-1}



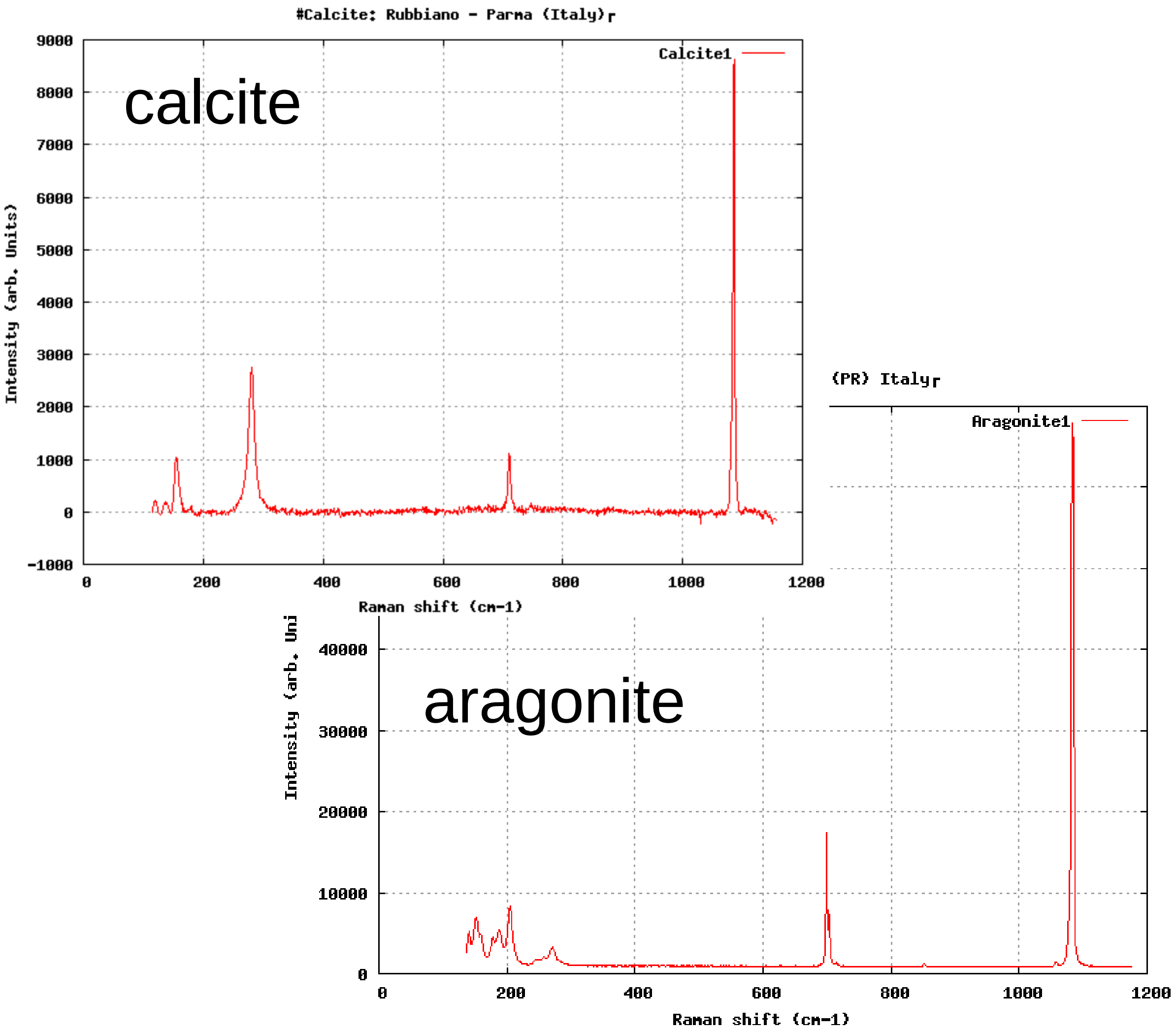
Raman spectrum of red lead 700 - 100 cm^{-1}

Basic Principles of Raman Spectroscopy

What Can Raman Do for Me?

Polymorph ID

- $CaCO_3$
- Calcite vs. aragonite
- Single chemical compound many crystal structures, atomic positions, phases



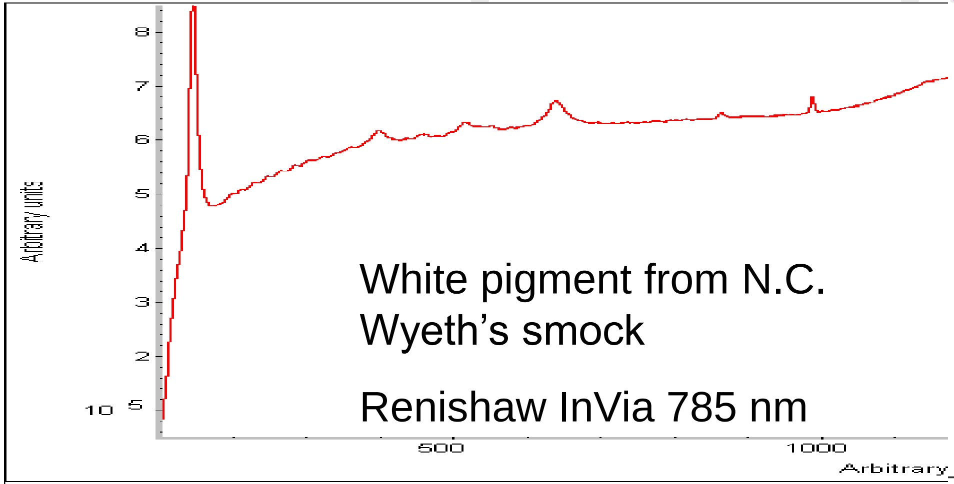
Confocal Labram multichannel microspectrometer Jobin-Yvon ltd. 514.5 nm excitation line Ar+ ion laser.

https://www.fis.unipr.it/phevix/ramandb.html

Basic Principles of Raman Spectroscopy

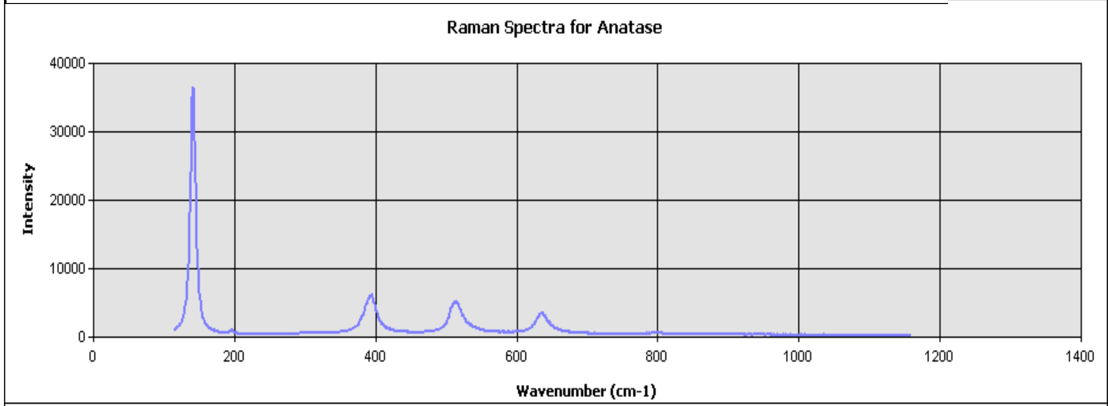
What Else Can Raman Do for Me?

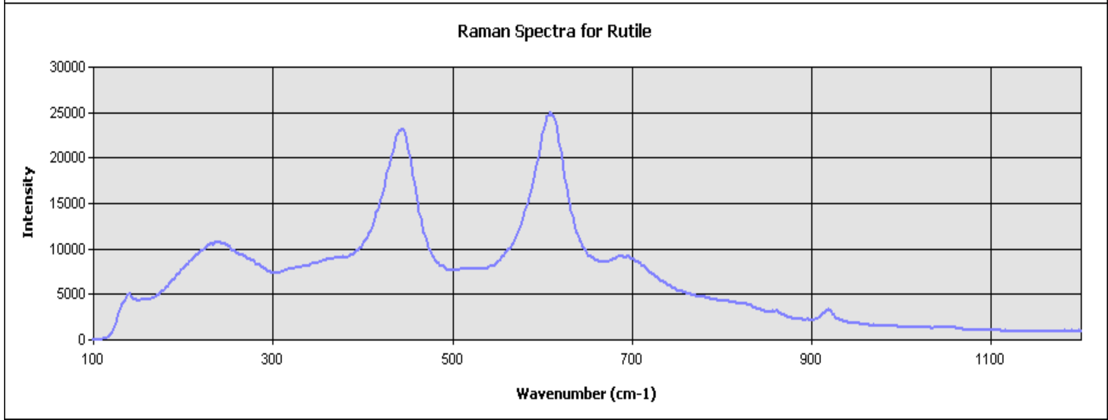
- White paint layer
- Ti present
  - TiO_2
  - Anatase vs. rutile?
- 1906 – anatase production
- 1937 industrial scale rutile production



White pigment from N.C. Wyeth's smock

Renishaw InVia 785 nm


Raman Spectra for Anatase


Raman Spectra for Rutile

Basic Principles of Raman Spectroscopy

Qualitative Analysis

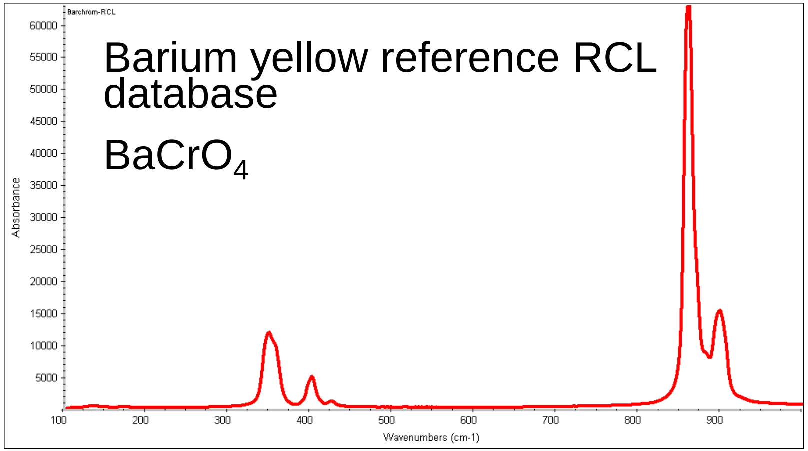
- What is in my sample?
  - Yellow N.C. Wyeth paint
  - Cd, Ba, Cr, Fe, Zn
  - Yellow pigments present?
    - $BaCrO_4$
    - $4ZnO\cdot{}_4CrO_3\cdot K_2O\cdot 3H_2O$
    - CdS
    - $Fe_2O_3.H_2O$+clay

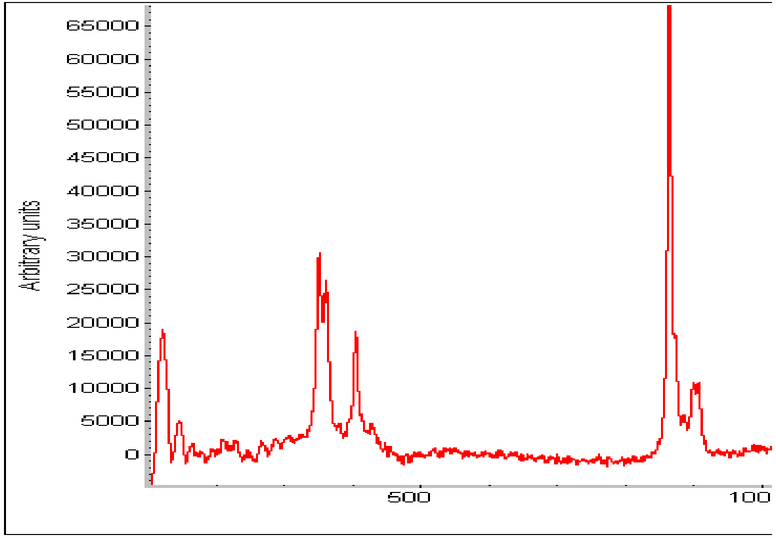
Measured vs. Reference Ba yellow

885, 899, 906, 864, 872, 350, 360, 404 cm^{-1}

885, 900, 907, 864, 873, 351, 361, 404 cm^{-1}

(http://www.chem.ucl.ac.uk/resources/raman/index.html)





(514 nm excitation)

Basic Principles of Raman Spectroscopy

Applications in Architectural Conservation

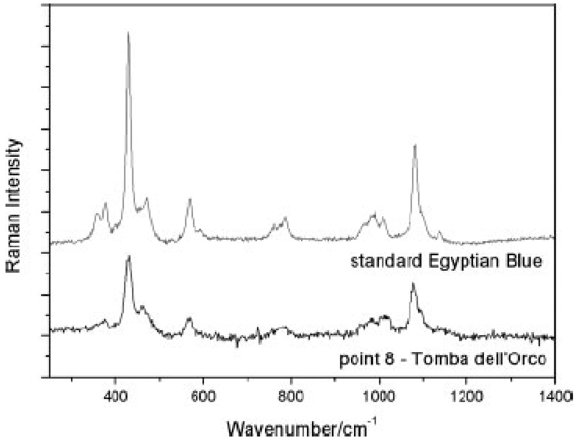


Figure 7. Comparison between the Raman spectra collected from a blue area (point 8 – Menelaus blue dress) and standard Egyptian Blue. The spectra are arbitrarily stacked for a better

Yellow and Blue Pigments

Figure 5. Particulars of Orco II, detail of the investigated yellow zones (on-line colour). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

Sodo, Armida; Artioli, Domenico; Botti, Alberto; DePalma,Giovanna; Giovagnoli, Annamaria; Mariottini,Maurizio; Paradisi, Alessandra; Polidoro, Costantino; and Ricci, Maria Antonietta.
The colours of Etruscan painting: a study on the Tomba dell'Orco in the necropolis of Tarquinia.
Journal of Raman spectroscopy 39(8) (2008): 1035-1041.

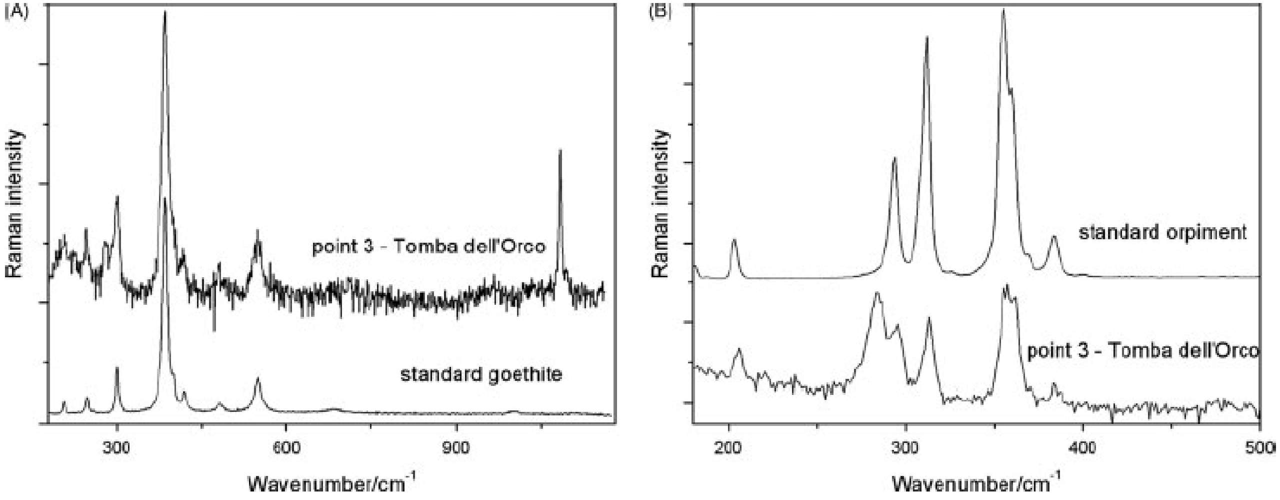


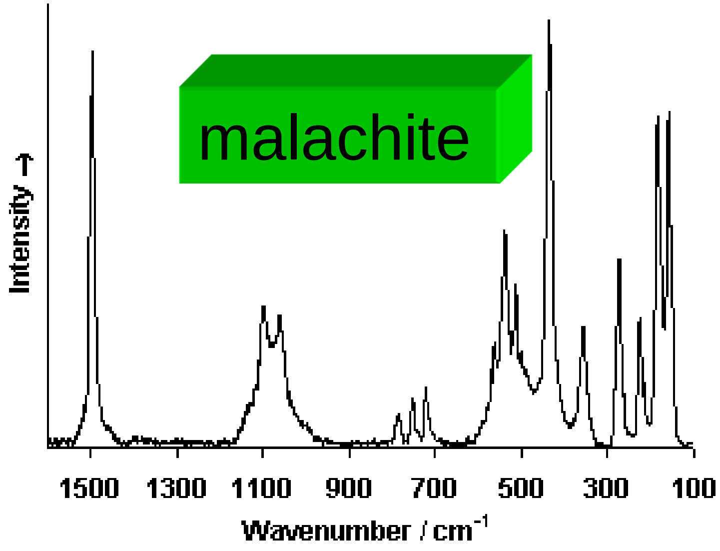
Figure 6. Comparison between the Raman spectra collected from a yellow decoration (point 3) and standard goethite (A) and between the Raman spectra of the cross-section of a yellow pigment (point 4 – Persephone hair) and standard orpiment (B). Spectra are arbitrarily stacked for a better visualisation.

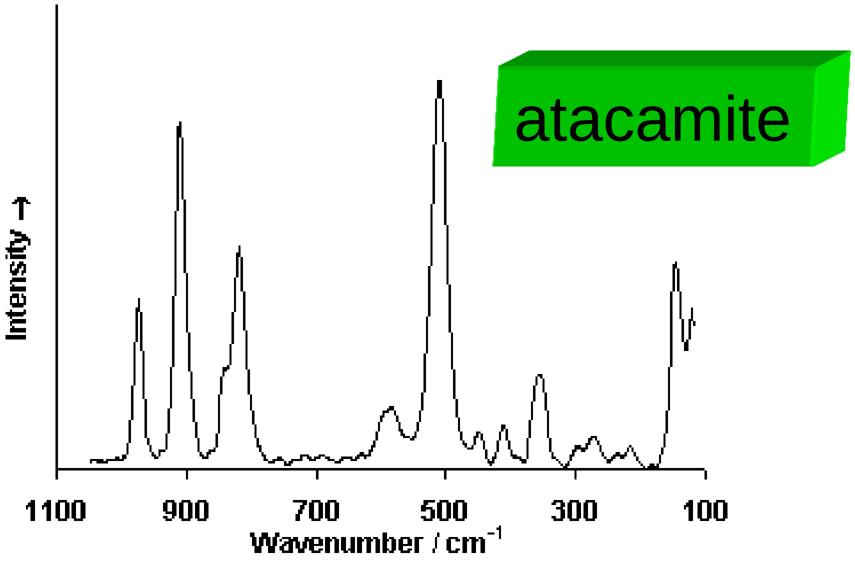
Basic Principles of Raman Spectroscopy

- Analysis of inorganic materials
- Pigments, corrosion products, glasses, minerals, gemstones, polymorphs, allotropes, salts, efflorescences, grounds, boles, fills, etc.
- Pale green copper corrosion - bronze disease? Atacamite $Cu_2Cl(OH)_3$ or malachite $CuCO_3 \cdot Cu(OH)_2$

Photograph courtesy of the Western Australian Museum

(514 nm laser excitation)





Basic Principles of Raman Spectroscopy

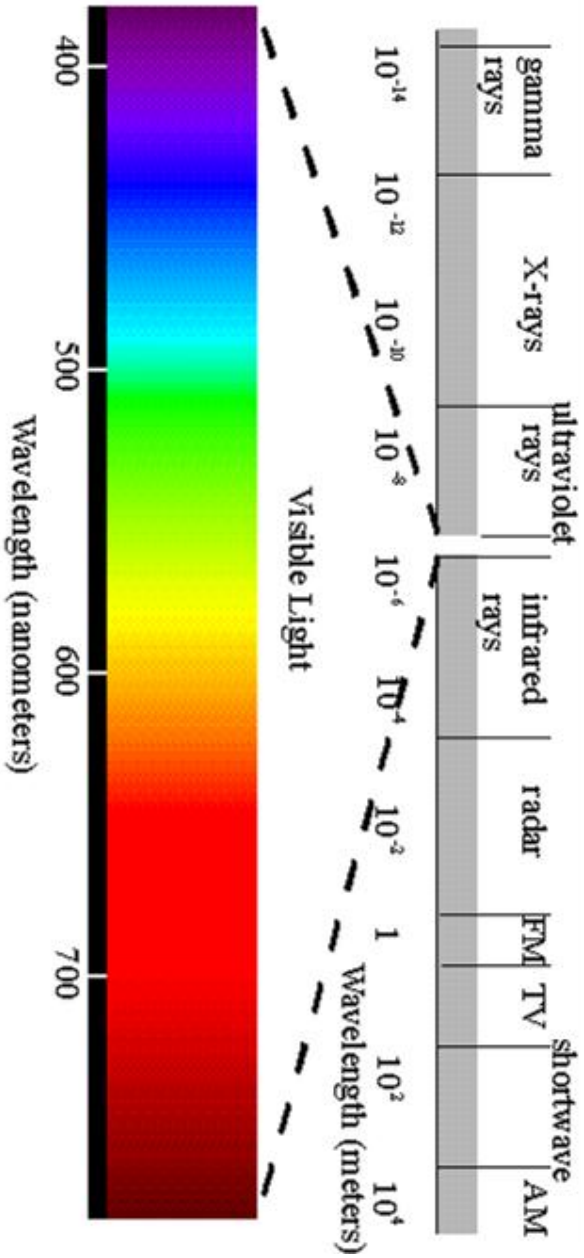
- Spectroscopic technique
  - Molecules interact with electromagnetic radiation (EMR)
  - Vibrational energy level gaps are probed
- Light scattering technique
- Sample irradiated with powerful laser

  monochromatic radiation (1 λ)

  UV light: 200 - 400 nm

  Vis: 400 - 700 nm

  NIR: 750 - 1400 nm
- Commonly used laser sources
  - 514 nm (argon), 633 nm (He-Ne), 785 nm (diode), 1064 nm (Nd:YAG)



Basic Principles of Raman Spectroscopy

What happens when laser hits your sample?

Absorbed, reflected, scattered, transmitted

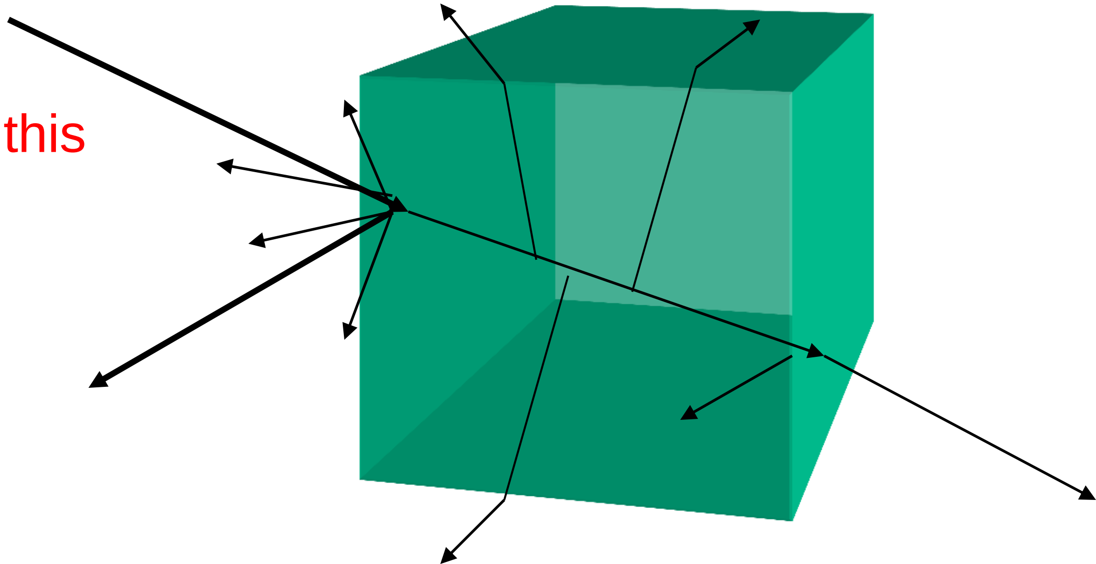
- Scattering
- Almost all scattering = Rayleigh scattering
- Incident λ= scattered λ
  - Elastic scattering
  - No molecular data in this

Specular reflection

Diffuse reflection

Scattering

Transmission



Basic Principles of Raman Spectroscopy

- Rayleigh scattered light - Incident λ = scattered λ
- **Raman scattered light – scattered λ ≠ incident λ**
  - **Inelastic scattering**
- Rayleigh scattering causes blue sky, red sunset

Daytime sky is blue:

Air molecules scatter blue light from sun (more than red light, shorter λ more strongly scattered)

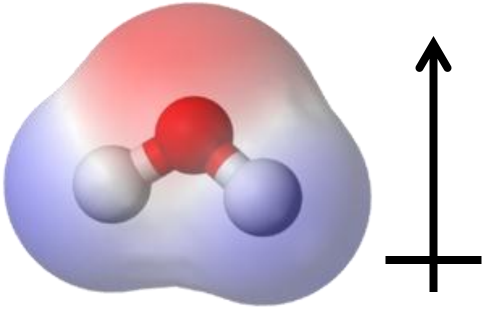
Sun at sunset: red and orange colors - blue light scattered out and away from the line of sight.

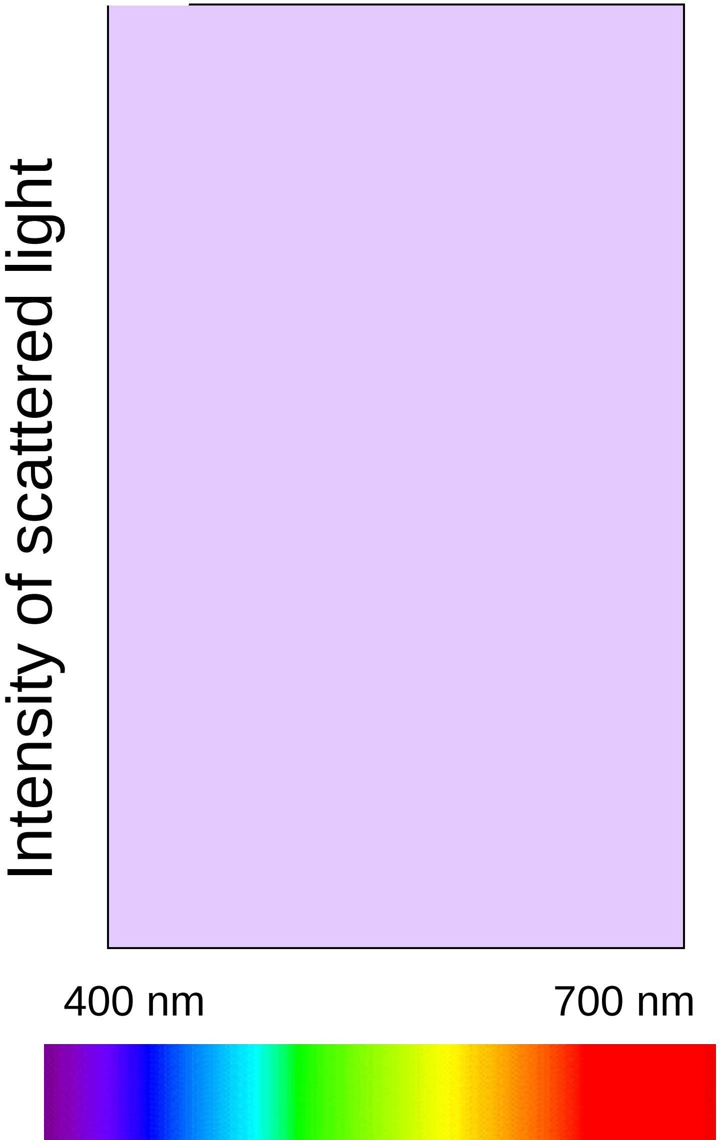
Basic Principles of Raman Spectroscopy

- Scattering strongly λ dependent –

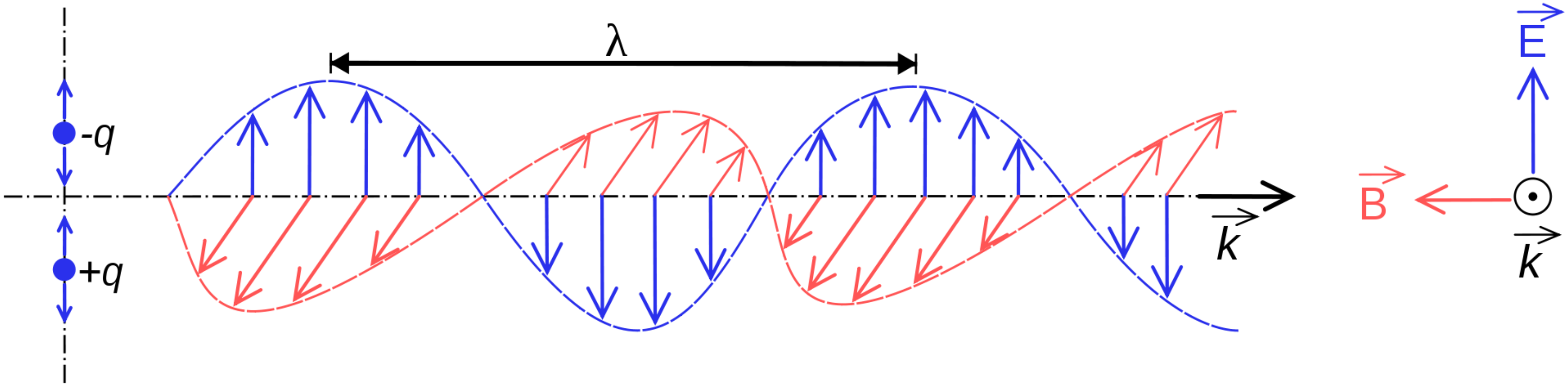
$$I_s/I_o \text{ proportional to } 1/\lambda^4$$

- Shorter λ more strongly scattered
- Molecules scatter light because EMR induces temporary dipole moments in them
- Dipole moment - unevenness of charge distribution in a molecule





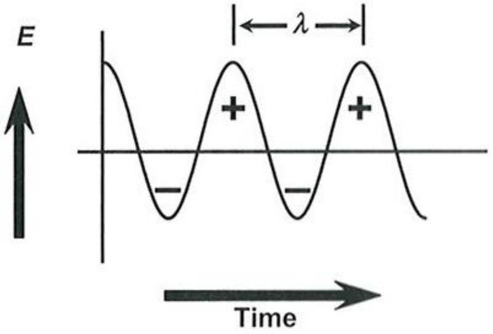
Basic Principles of Raman Spectroscopy



Interaction with electromagnetic radiation

1. Oscillating perpendicular electric and magnetic fields
2. Electric field component interacts with molecule
3. Important parameters:
   - λ = length of one wave
   - Wavenumbers = number of waves per unit length = $\bar{\nu}$
   - c = speed of light
   - n = index of refraction of medium
4. E = hν

   h = Planck’s constant 6.6256 x 10^{-27} erg sec

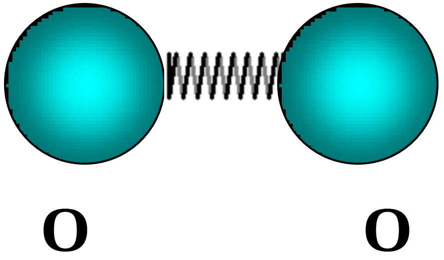


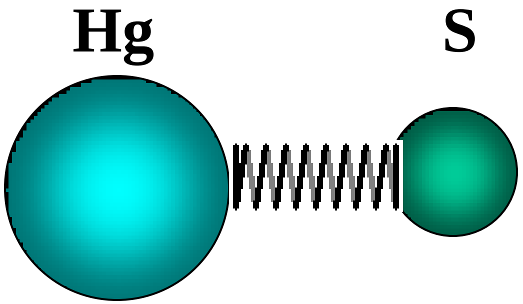
$$\bar{\nu} = \frac{\nu}{(c/n)} = \frac{1}{\lambda}$$

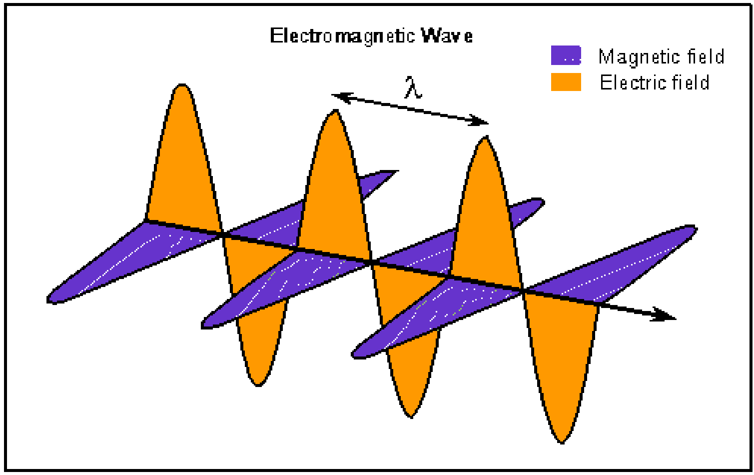
Basic Principles of Raman Spectroscopy

Raman experiment

1. Electric field component of incident EMR interacts with molecule
2. Fluctuating field induces **temporary dipole moment**
   - Asymmetric distribution of charges
   - Molecule's **polarizability** determine's strength as Raman scatterer
   - Note: IR has different rules – a change in amplitude of **existing dipole moment** must occur.



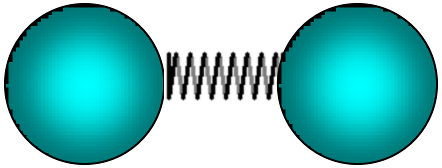




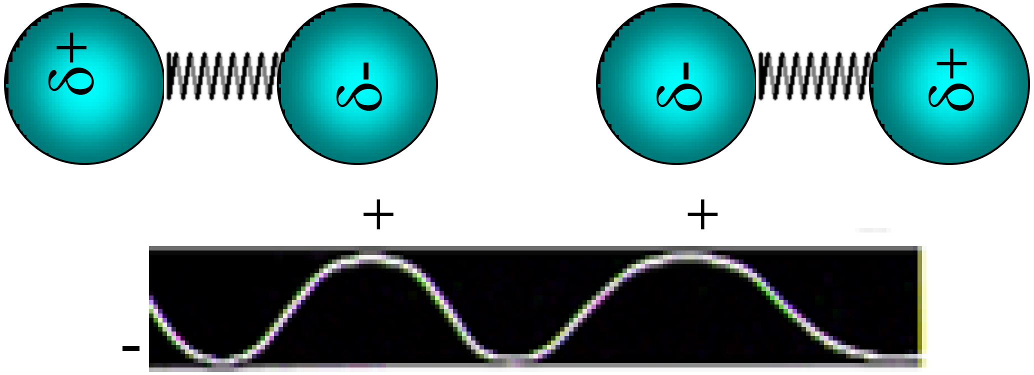
http://www.astronomynotes.com/light/s2.htm

Basic Principles of Raman Spectroscopy

- Fluctuating electric field induces temporary dipole moment
  - Asymmetric distribution of charges
  - Electrons and protons ‘pulled’ in opposite directions in electric field
  - Induced dipole moment caused by incident radiation
    - This fleeting/temporary electronic state generates Rayleigh and Raman scattering
    - Forms ‘virtual’ electronic energy level



No electric field

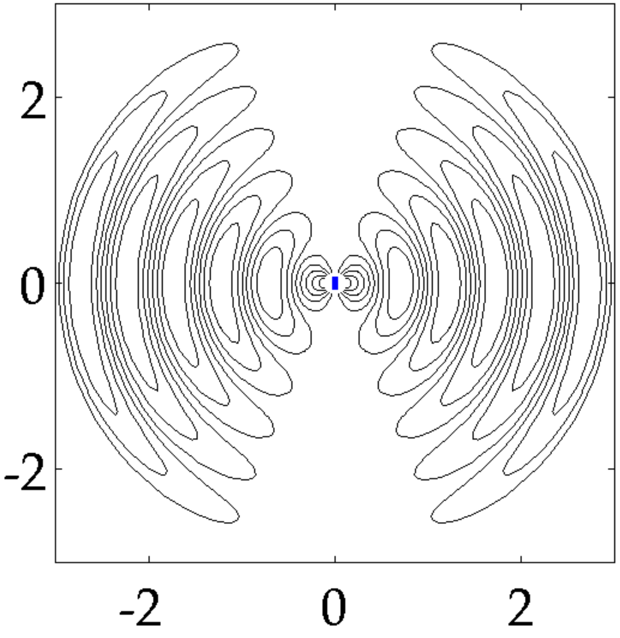


Electric field vector of incident light

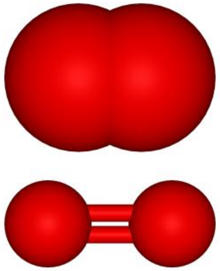
Molecule experiences oscillating charges

Basic Principles of Raman Spectroscopy

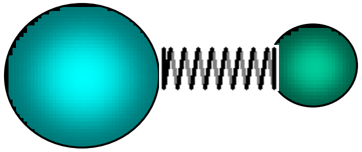
- The Raman scattering process:
- Oscillating electric field (of incident EMR) induces oscillating dipole in molecule
- Oscillating dipole in molecule causes it to emit EMR
- Scattering can be thought of as an absorption and re-emission process
- Degree of induced dipole moment result of molecular polarizability – how much can the electron cloud be deformed?



Electromagnetic Waves and Antennas
Sophocles J. Orfanidis

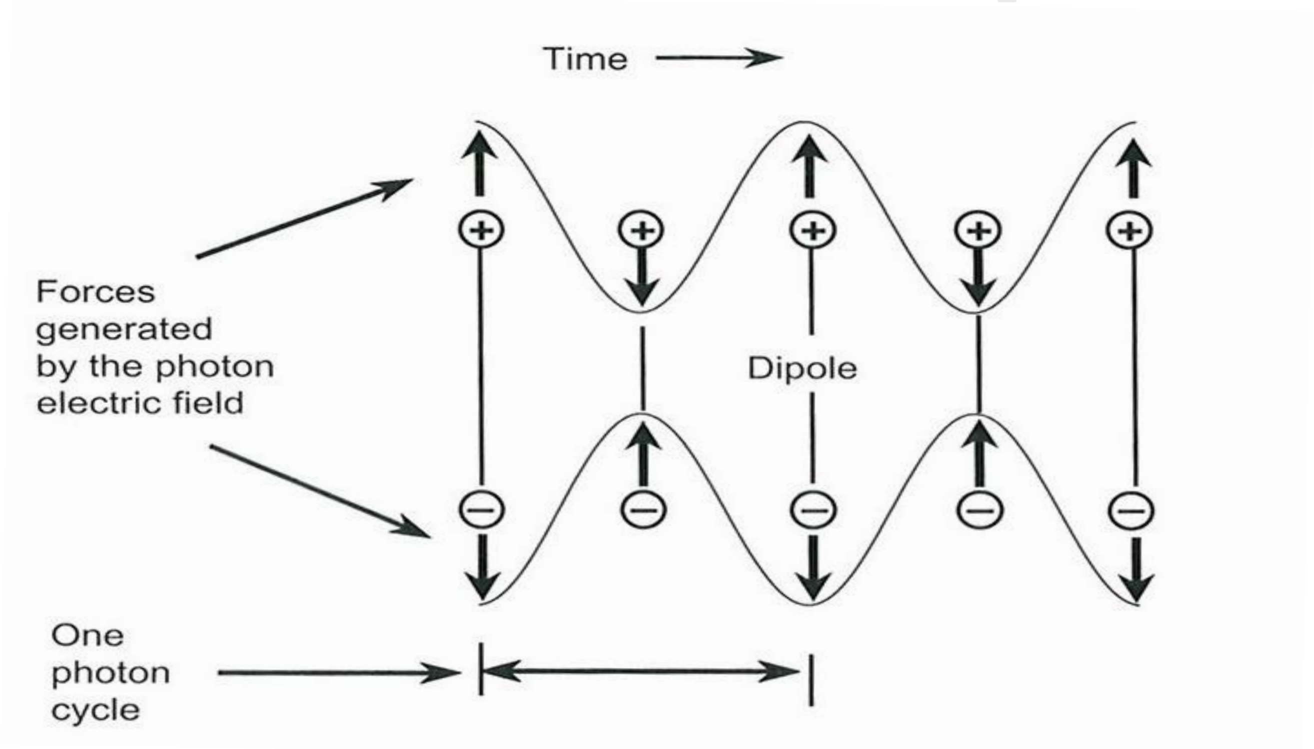


O=O



Hg - S

Basic Principles of Raman Spectroscopy

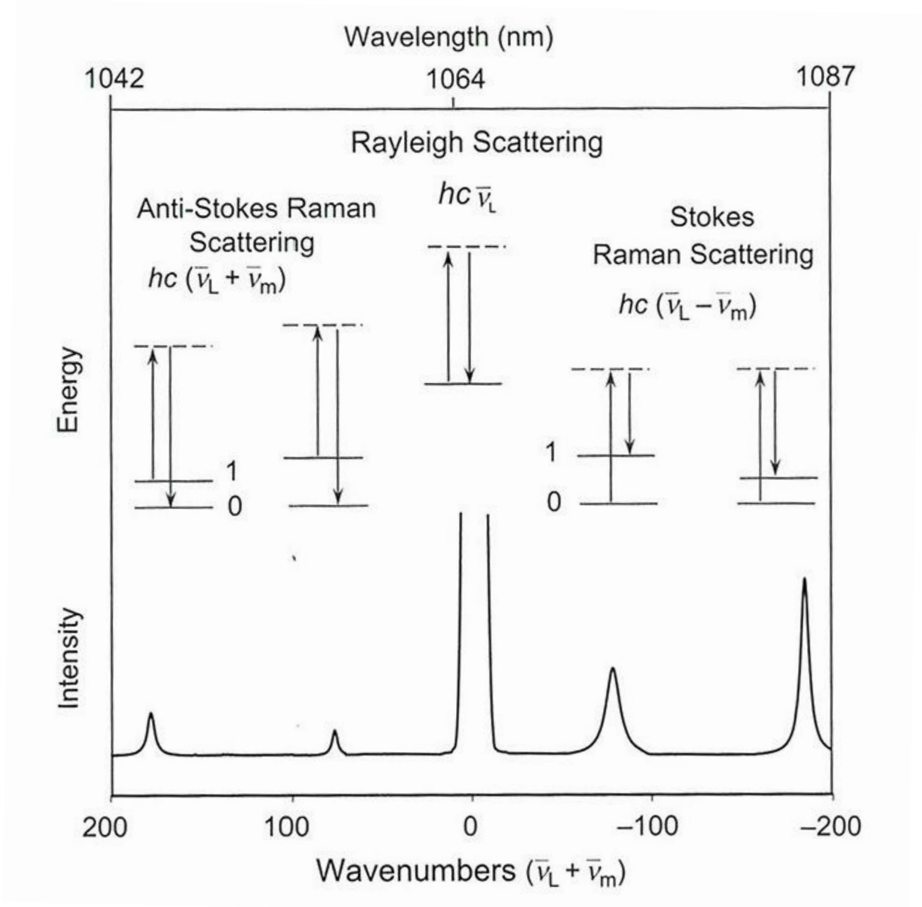


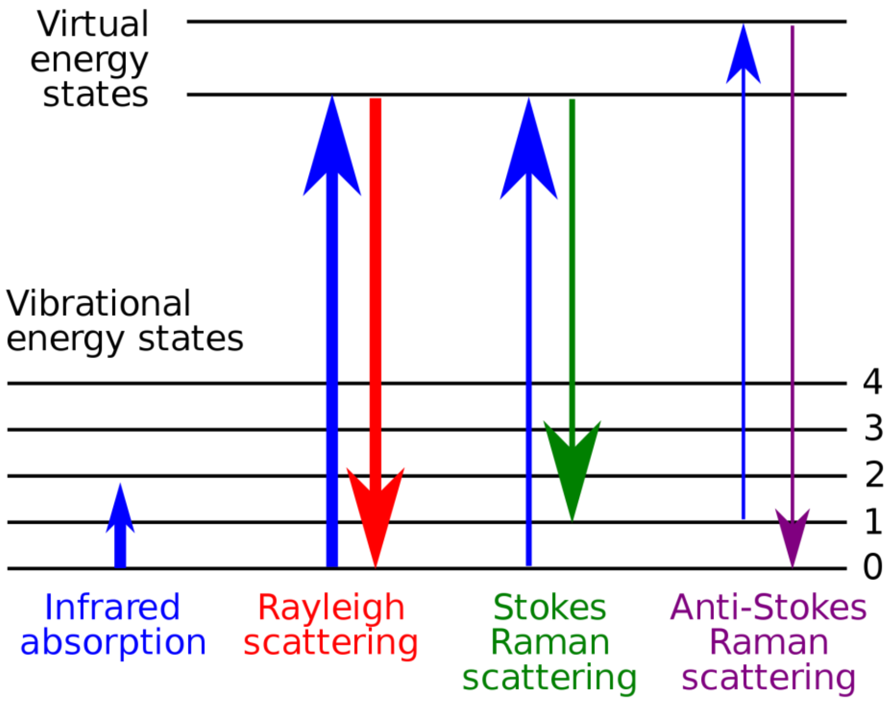
- Comparison to IR mechanism
- Molecular dipole moment required
- Oscillating frequency of EMR matches natural frequency of one of the molecule’s normal modes of vibration
  - Leads to an absorption
- For energy transfer from photon to molecule vibration must cause change in dipole moment
  - Vibration will be IR active

Basic Principles of Raman Spectroscopy

- **Most scattered photons will be Rayleigh light**
  - **No energy lost during scattering**
  - **Elastic scattering**
  - **Intensity ~ 10^{-3} less than incident**
- **Small amount will be Raman**
  - **Some energy lost to vibrational changes that cause a change in polarizability**
  - **Inelastic transition between photon and molecule**

Full Raman spectrum including Rayleigh and anti-Stokes lines





Images from UC Davis Dept of Chem. and IR and Raman Spectroscopy, Peter J. Larkin

Basic Principles of Raman Spectroscopy

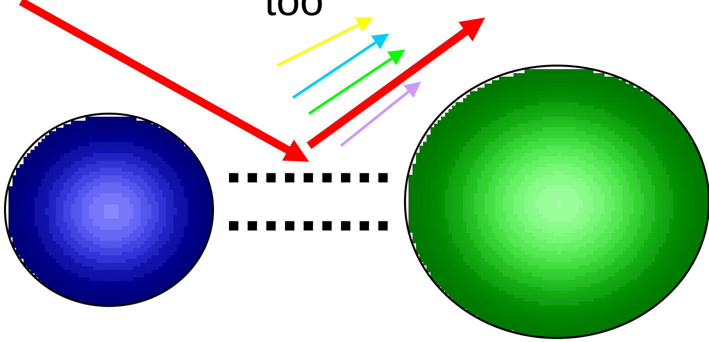
REMEMBER
$E=h\nu = hc/\lambda$
h = Planck's constant
c = speed of light in vacuum

Basic Experiment:

- Sample irradiated with laser – monochromatic radiation
- Spectrum of scattered radiation measured

- Raman scattering
  - Incident $\lambda \neq$ scattered λ
- ΔE = vibrational energy level gaps

$\Delta \lambda$ = (incident and scattered wavelengths) correspond to wavelengths in mid-IR



785 nm diode laser light

Almost all Rayleigh scattering

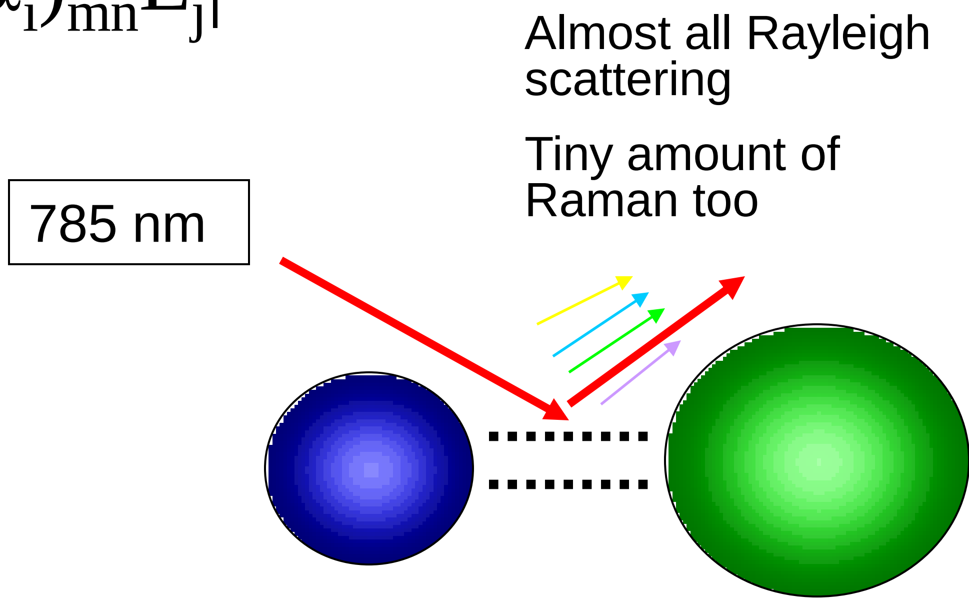
Tiny amount Raman too

- **NOTE: Raman line intensity = or < 0.000001x Rayleigh intensity (not including competition from fluorescence)**

Basic Principles of Raman Spectroscopy

- **How much Raman scattering will we see?**
  - Scattered light intensity (vibrational transition m to n)

$$I_{n \leftarrow m} \infty N(\nu_0 \pm \nu_{nm})^4 \sum_{i,j} |(\alpha_i)_{mn} E_j|^2$$



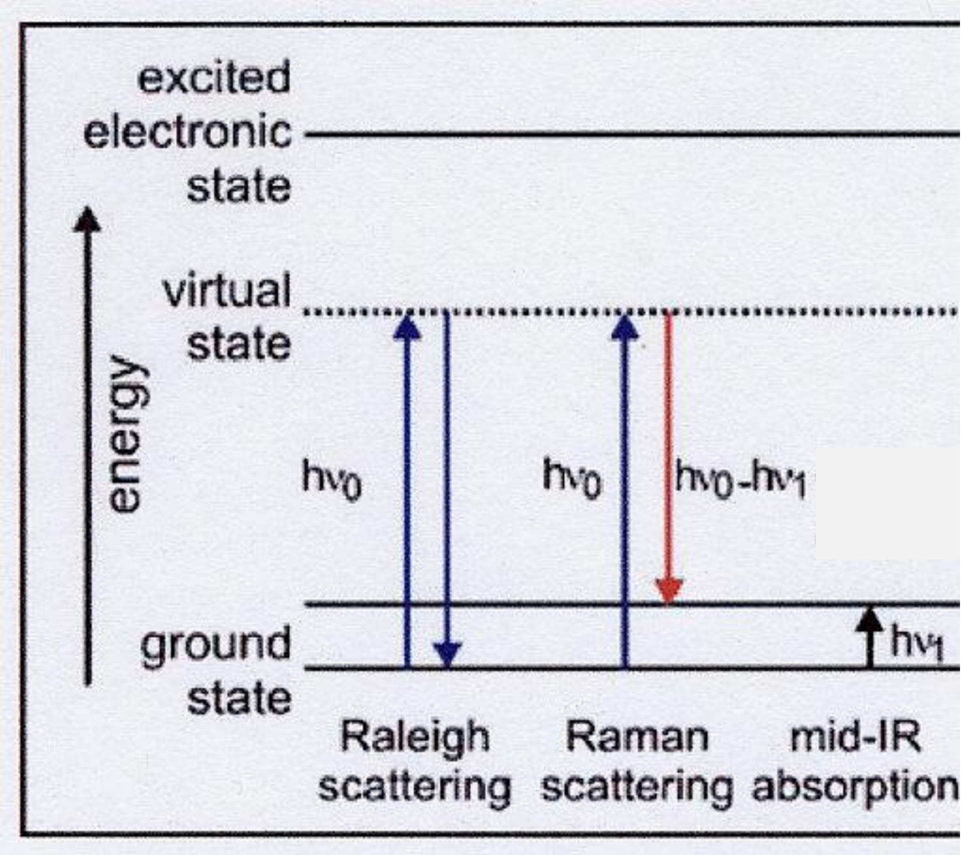
785 nm

Almost all Rayleigh scattering

Tiny amount of Raman too

N	Number of molecules
ν_0	incident light frequency
ν_{mn}	vibration frequency
$(\alpha_i)_{mn}$	polarizability
E	Electric field strength (laser power)

Basic Principles of Raman Spectroscopy



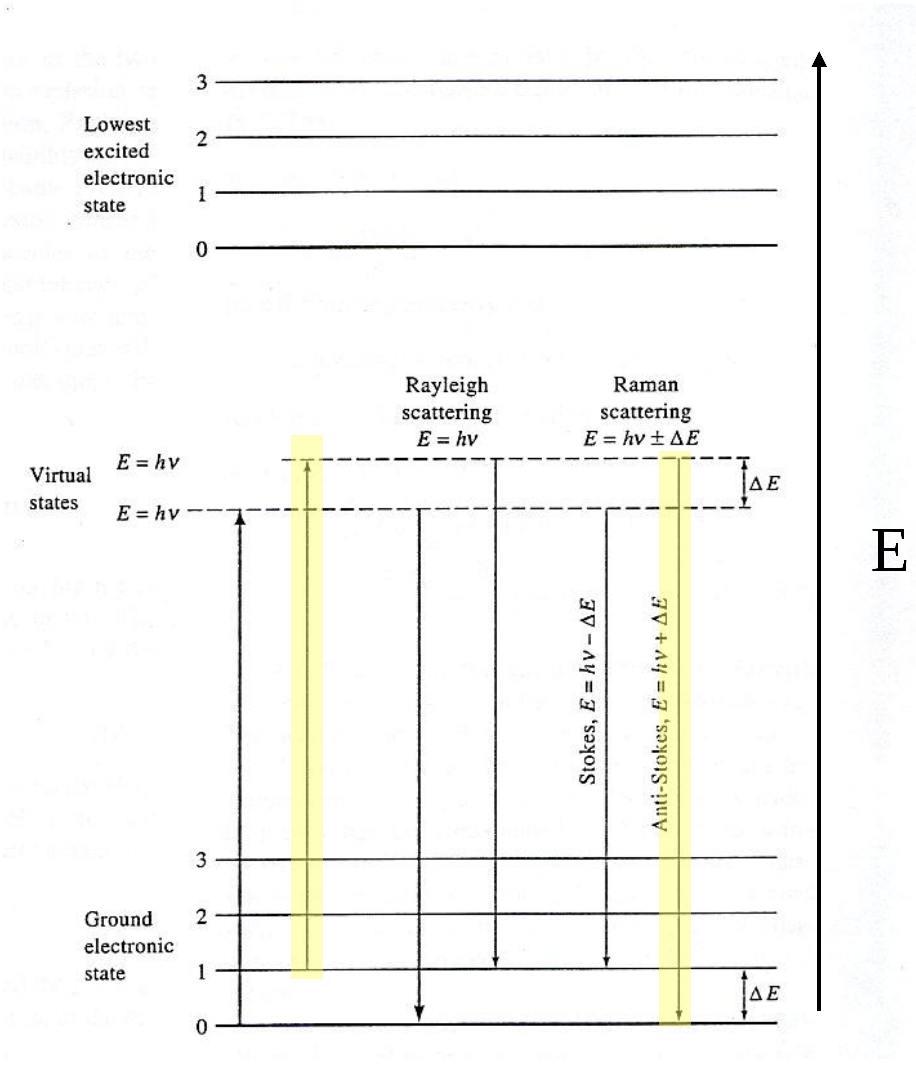
Remember:
E = hν

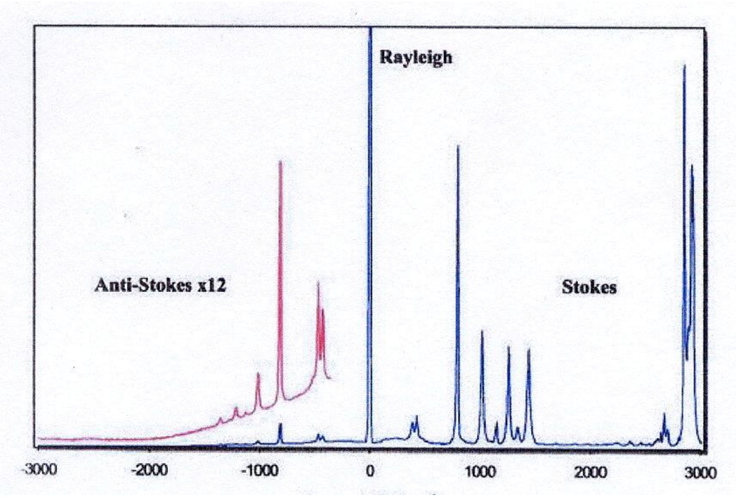
Raman transition shown here = Stokes line

- Incident λ ≠ scattered λ for Raman
- ΔE = vibrational energy level gaps of molecule
- Stokes line, Raman scattered radiation has longer λ, smaller E, smaller ν
  - Most commonly observed – most molecules at vibrational ground state at RT

Basic Principles of Raman Spectroscopy

- Anti-Stokes lines – smaller λ, higher E and ν than incident





Anti-Stokes low intensity

Why? most molecules in vibrational ground state at room temperature

Rayleigh has no information and anti-Stokes rarely used

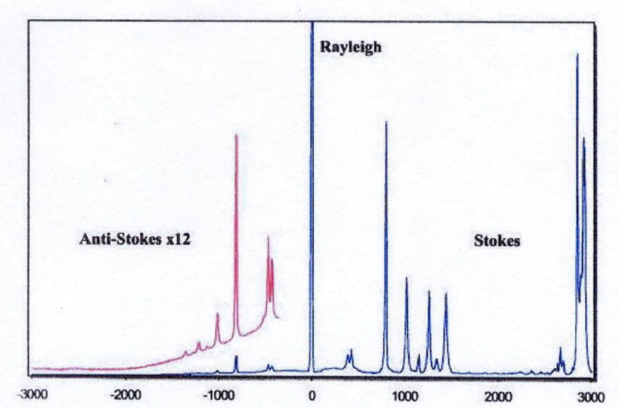
Spectrometer filters remove Rayleigh + anti-Stokes lines

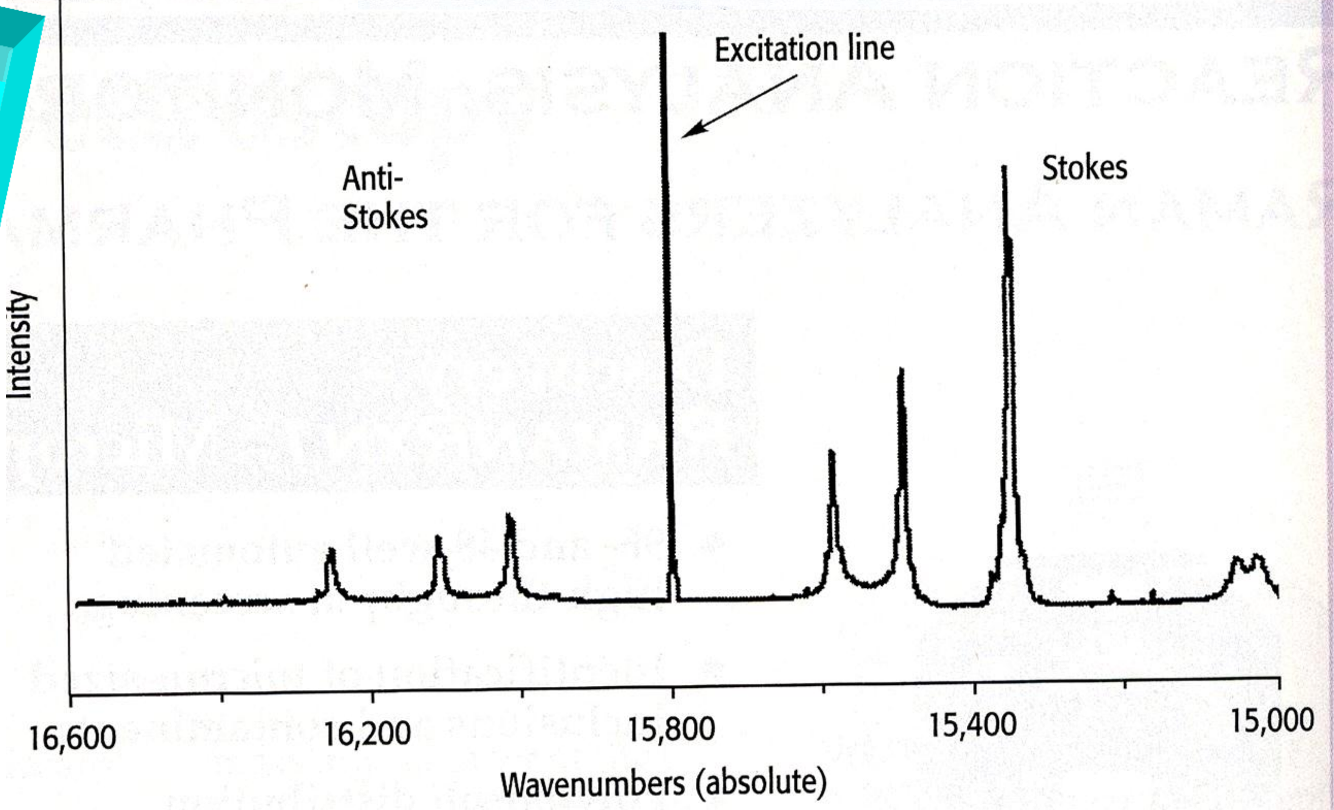
Basic Principles of Raman Spectroscopy

- ΔE = energy gap between vibrational energy levels of molecule

Rayleigh line set at Raman shift = 0

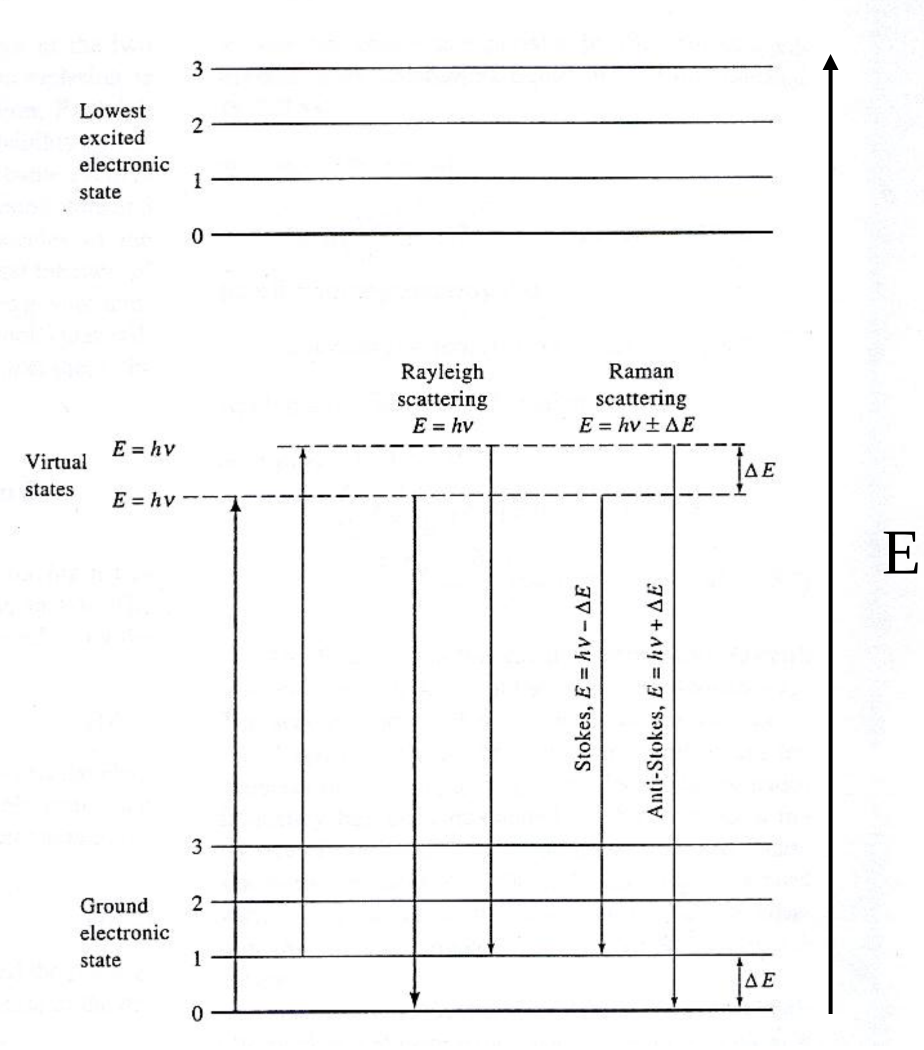
Note that ν of scattered Raman radiation independent of exciting radiation ν





Basic Principles of Raman Spectroscopy

- Selection Rules



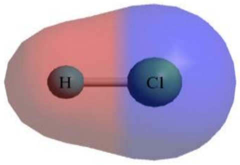
Allowed Raman vibrational modes:

- cause a change in polarizability of the molecule

Ability to induce dipole moment

– distortion of electron cloud

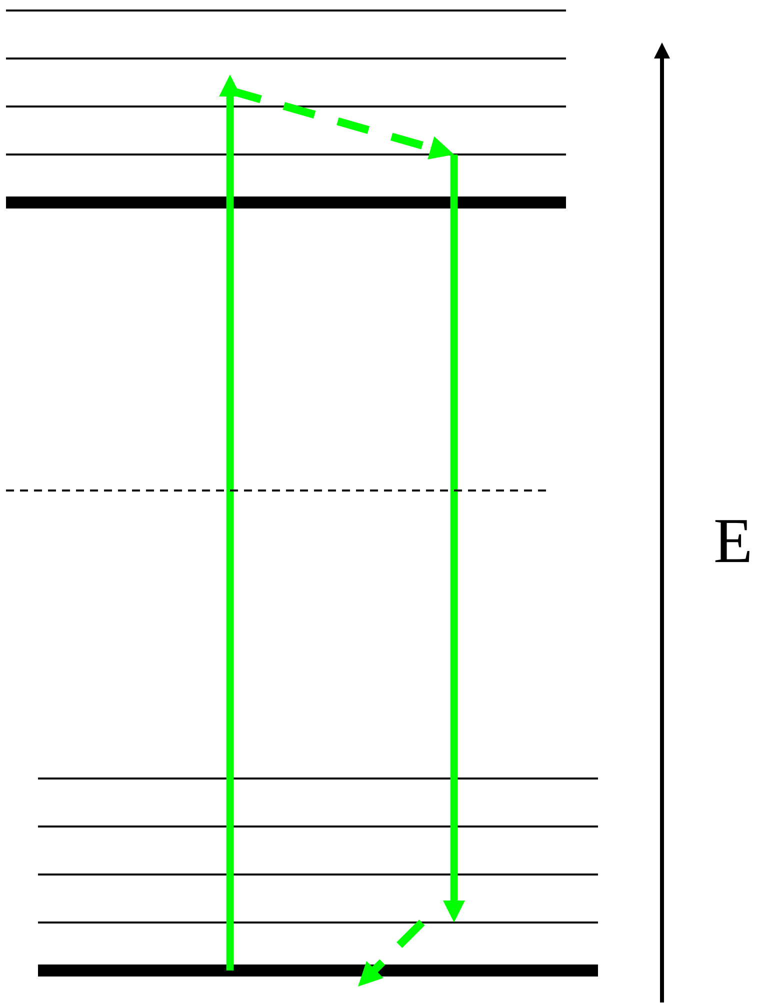
Vibration is IR active if there is a change in permanent dipole moment during vibration



Basic Principles of Raman Spectroscopy

Competing Effect – Fluorescence

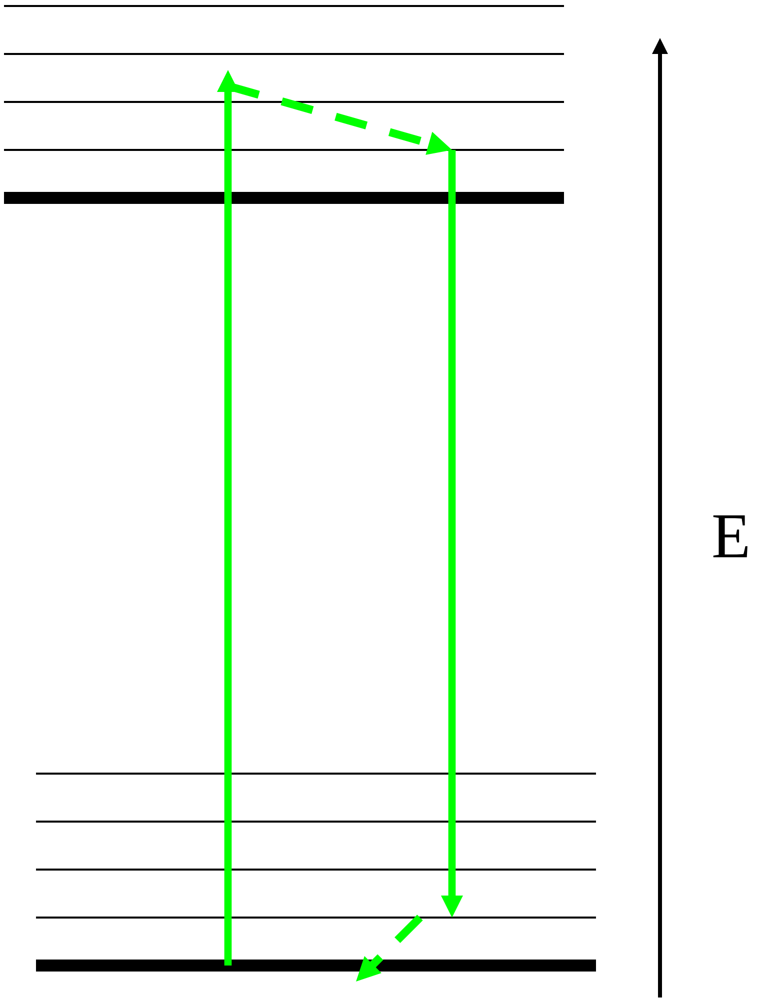
- Excitation to 1st excited electronic state, excited vibrational state within that electronic state
- Radiationless/relaxation to lower vibrational state
- Relaxation back to ground electronic state
- Radiationless relaxation to lowest vibrational state



Basic Principles of Raman Spectroscopy

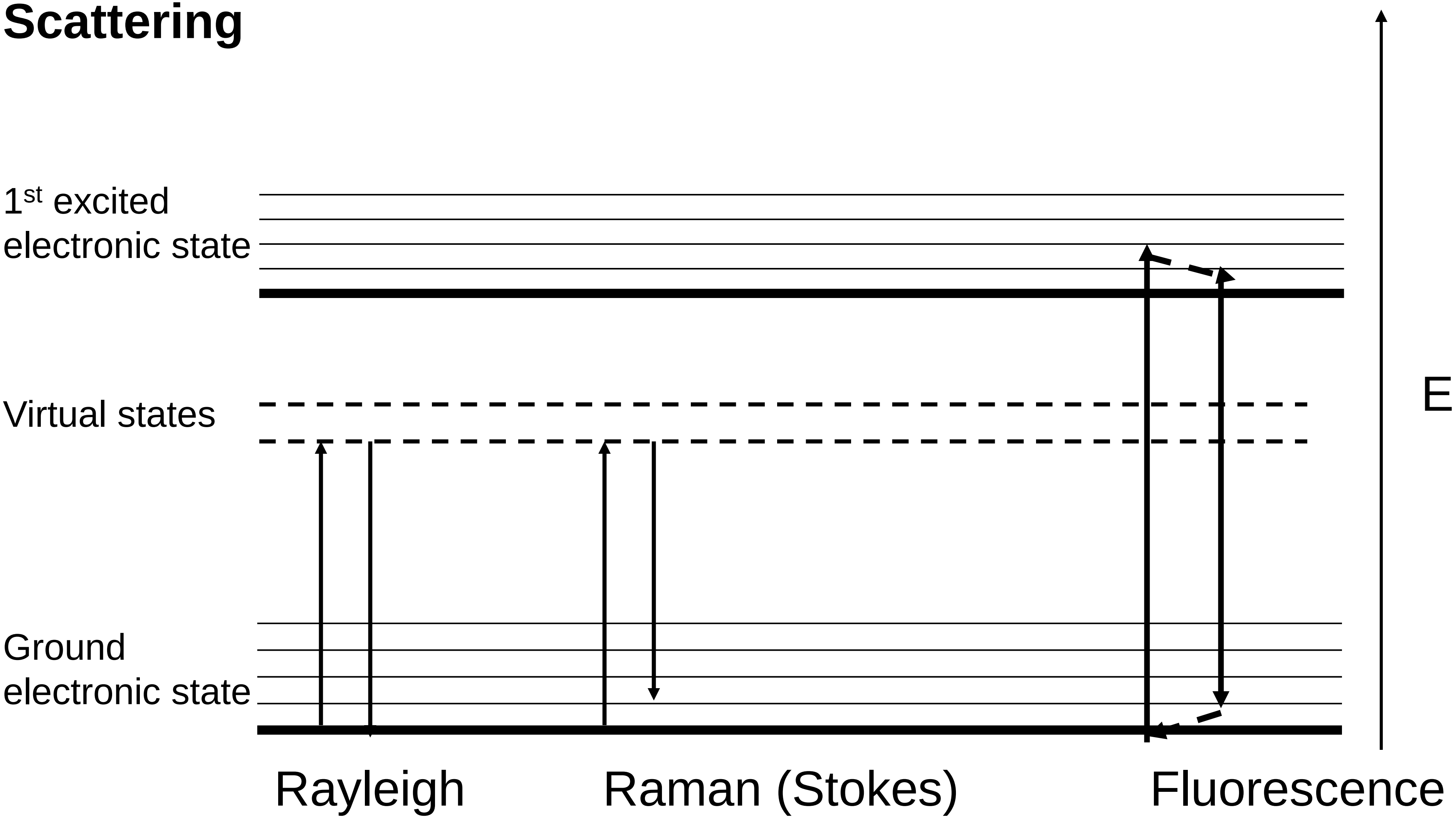
Competing Effect – Fluorescence

- From analyte, matrix, impurities
- Oil binders are particularly problematic
- Can increase scattering by going to shorter excitation λ, but increase fluorescence too
  - For every 1×10^6 Rayleigh scattered photons there is ~1 Raman photon
  - For every 1 Raman photon there can be 1×10^3 fluorescence photons



Basic Principles of Raman Spectroscopy

Three Competing Effects: Fluorescence, Rayleigh, Raman Scattering



1st excited electronic state

Virtual states

Ground electronic state

E

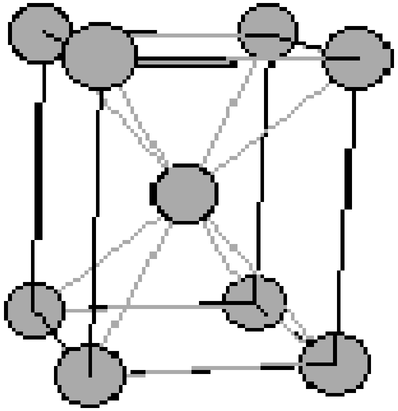
Rayleigh

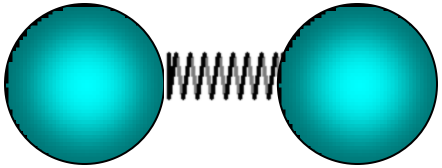
Raman (Stokes)

Fluorescence

Basic Principles of Raman Spectroscopy

- The Raman Experiment
  - Measure scattered light ν's (reported as cm^{-1})
  - Relate to functional groups in molecule
  - Match to Raman databases of artists' materials, minerals, polymers
  - Scattered ν's depend on:
    - Atoms present
    - Force constant (bond strength) between them
    - Crystal structure (phonons/ lattice vibrations measured)
    - Packing environment

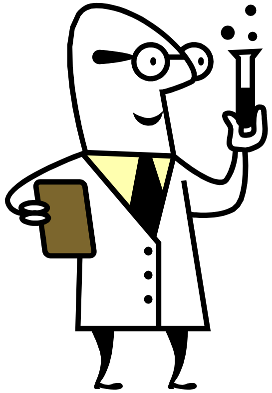


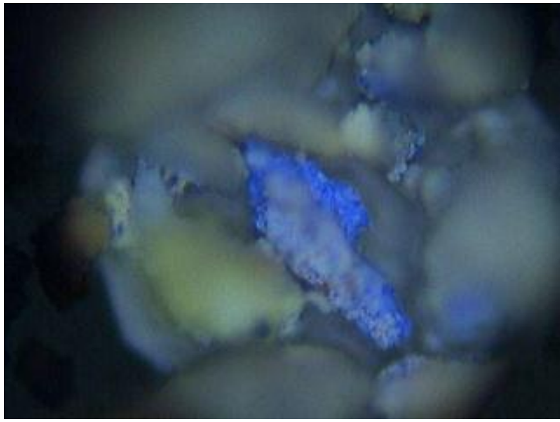


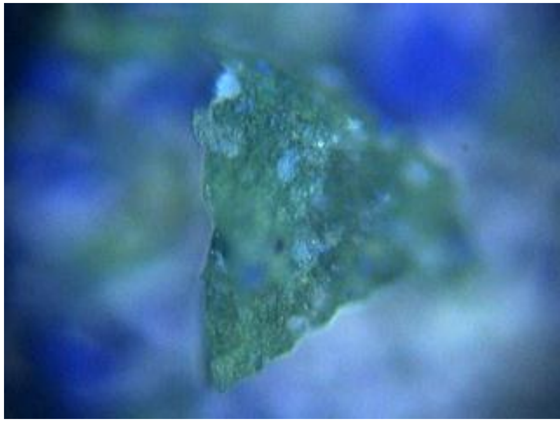
Basic Principles of Raman Spectroscopy

- **Sample Sizes/Concentrations**
  - for most paints:
    - Paint chip mounted in x-section
    - Single pigment particles
    - Laser spot size varies among instruments
      - Renishaw InVia 1 µm × 20 µm line or 1 µm diameter spot
    - 1 - 5 mg paint sample – can extract particles from oil binder using DMF followed by ethyl acetate rinses
    - *In situ* analysis: no sampling needed (fiber optic probe, 90º angle optic, open architecture)
      - May have to remove varnish
      - abrade surface to expose pigment particles

great sample size for conservation!







Basic Principles of Raman Spectroscopy

- **What laser wavelength do I use?**
  - **Too close to absorption band can lead to excessive fluorescence**
  - **But resonance Raman effects can be exploited too – enhancement**
  - **Conclusion: multiple wavelengths essential!**

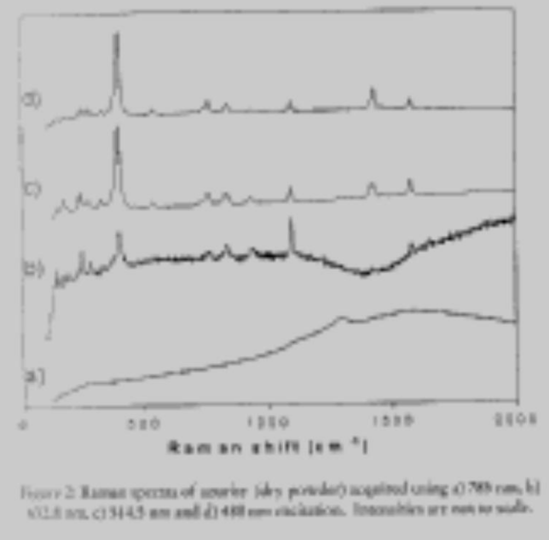
azurite

488 nm

514.5 nm

632.8 nm

785 nm

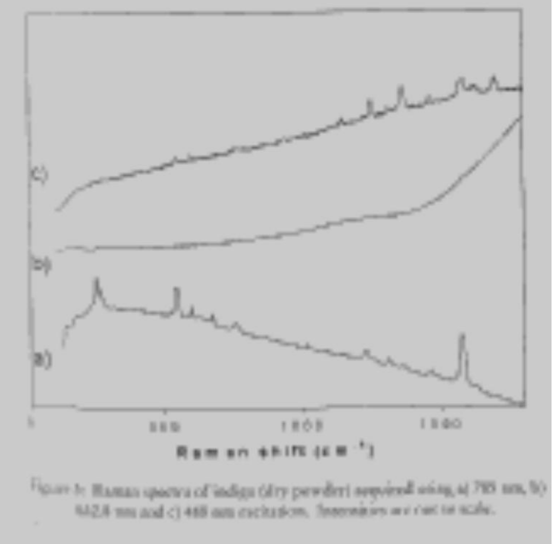


indigo

488 nm

632.8 nm

785 nm



Karen Trentelman and Carole Havlik, "Building a Multi-Dimensional Raman Database: The Effect of Excitation Wavelength and Binding Medium on the Raman Spectra of Artists' Pigments, Proceedings, ***The Sixth Infrared and Raman Users Group Conference (IRUG6)*** ed. Marcello Picollo, Florence, Italy, March 29th – April 1st 2004 p. 94-100.

Basic Principles of Raman Spectroscopy

Advantages – You can do amazing things with Raman

- Excellent sensitivity – single particle
- Inorganic and organic phase ID
  - non-crystalline material
  - minor components
- Definitive identification possible
- Can identify polymorphs (TiO_2 rutile vs. TiO_2 anatase)
- Much cheaper than XRD for microsamples
- Flexible (fiber optic probe, microscope stage, or 90º angle)
- Limited sample prep/analysis
  - paint cross-section, *in situ*, or DMF
  - Grind up corrosion if consolidant
- Inorganics - vibrational modes for M-ligand bonds typically between 100-700 cm^{-1}

Andy always knew he was destined for greatness.

No surprise he wound up a Raman specialist at **Jobin Yvon.**

The Raman Division at Jobin Yvon is ready to help you find your inner Raman greatness wit a comprehensive, broad selection of Raman instruments, software and services to get you up and running to maximum potential. Backed by 185 years of spectroscopic excellence and expertise we guarantee you will achieve Rama greatness with Jobin Yvon.

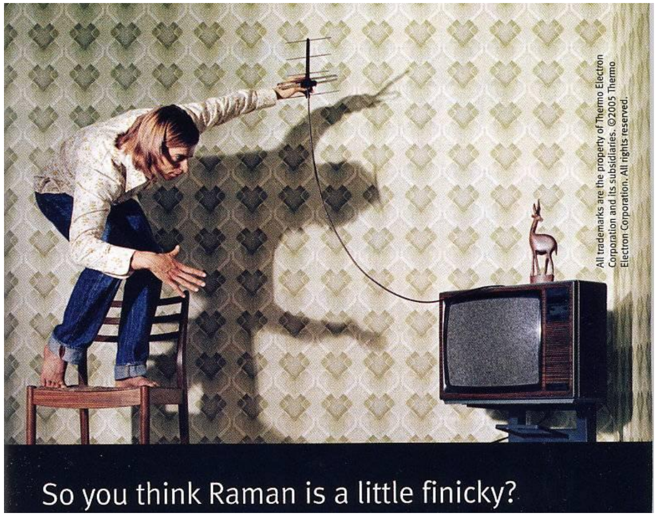
Whatever your Raman challenge, whatever your Raman question, our extensive team of Raman specialists are ready to provide the optimum Raman solution for **EVERY** situation Jobin Yvon has the largest selection of Raman instrumentation available from any company. So whether you want analytical, research or process Raman, Jobin Yvon is the right choice to obtain the best results.

Ready to learn more about our world renowne Raman offerings? Call us at **732-494-8660** or visit **www.jobinyvon.com** to unleash your Raman greatness. Cape not included.

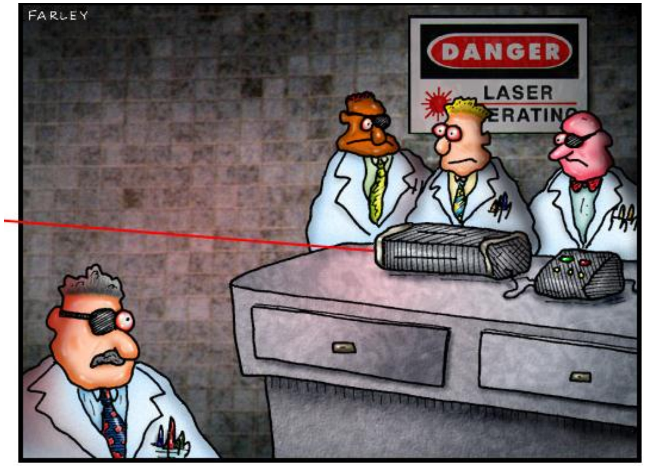
Raman Spectroscopy

Limitations

- Invasive and destructive sampling sometimes required
- Expensive ~ $180,000 for a system with 2 lasers
  - Multiple laser λ's needed
- Heating and decomposition of dark samples
  - Phase changes
- Fluorescence of analyte, matrix, or impurities can interfere with detection of Raman signal
- Laser safety considerations



So you think Raman is a little finicky?

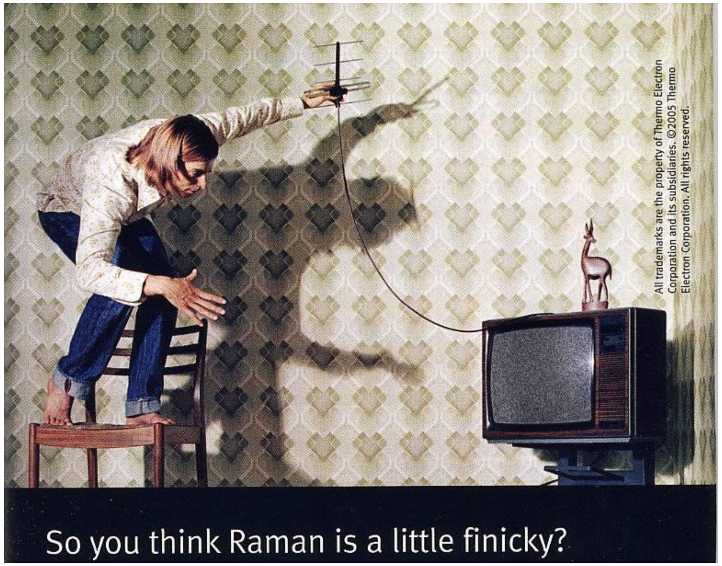


Peer pressure in the laser lab

Basic Principles of Raman Spectroscopy

Thanks to:

- Greg Smith (Indianapolis Museum of Art)
- Karen Trentelman (Getty)
- Sylvia Centeno (Metropolitan Museum of Art)
- Joe Weber (University of Delaware)
- Catherine Matsen (Winterthur)
- Rich Bormett (Renishaw)
- Fran Adar (JY Horiba)
- Beth Price (PMA) & IRUG



Infrared & Raman Users Group

Raman Spectroscopy Workshop

Overview of Raman instrumentation

Tom Tague

Bruker Optics, Billerica, MA, US

THURSDAY, SEPTEMBER 27: LECTURE 3

Overview of Raman Instrumentation

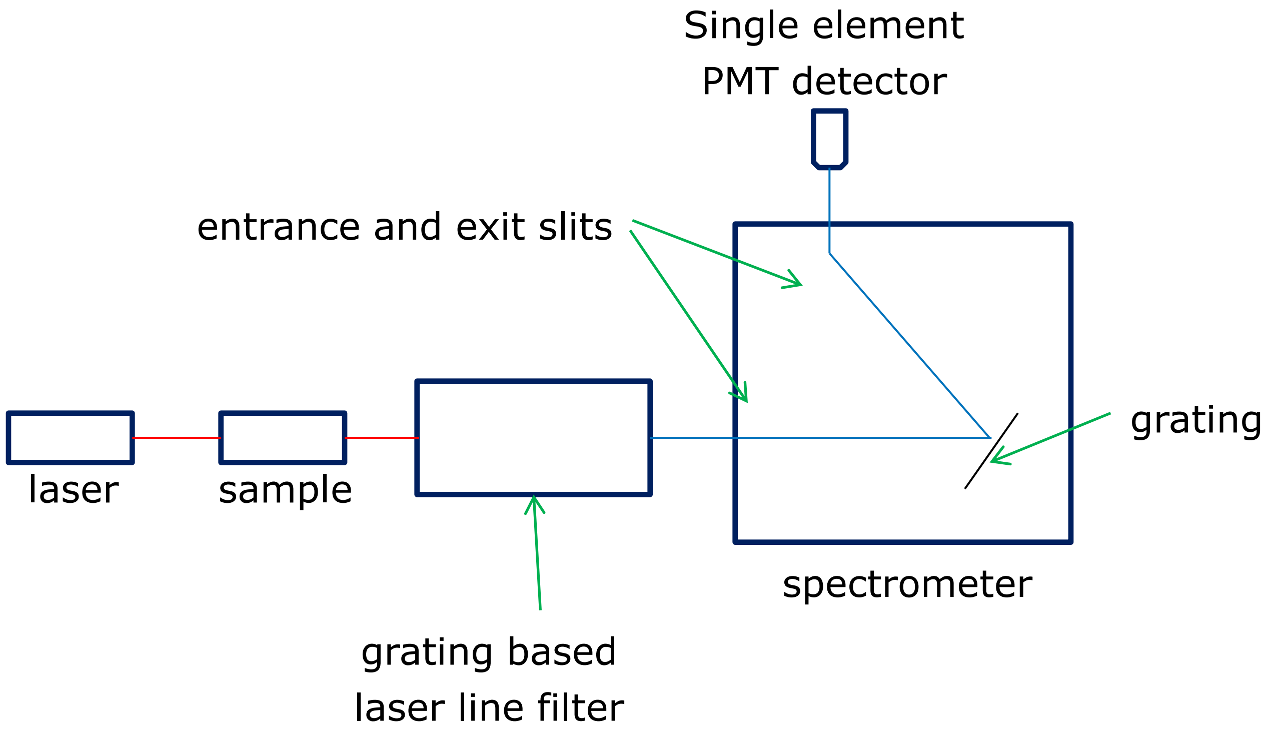
Tom Tague, Ph.D.

tjt@bruker.com

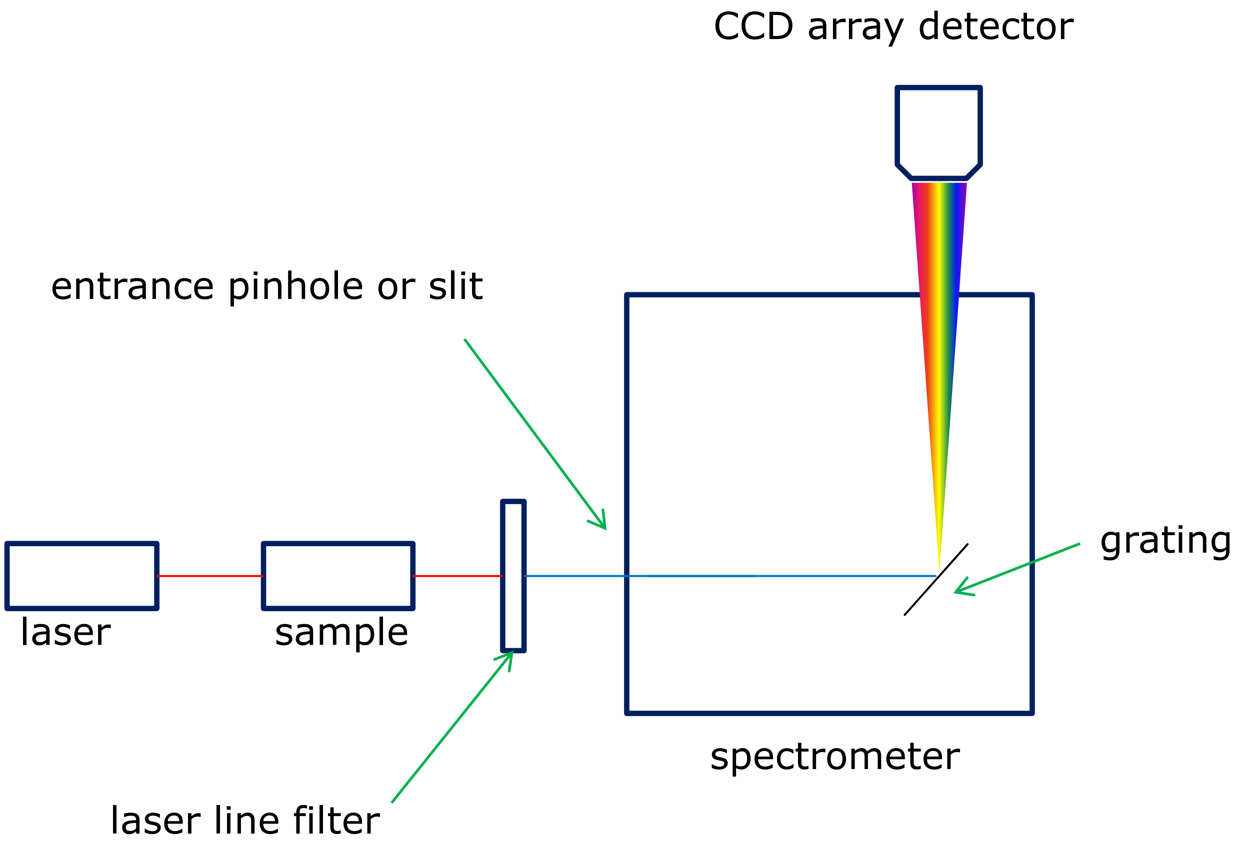
Raman instrumentation components

- Laser sources
- Neutral density filters (power selection)
- Entrance slits and pinholes
- Objectives
- Filters
- Gratings
- Detectors
- Calibration standards
- Video cameras
- Stages (manual, motorized, gantry, z-stage)
- Probes
- Handheld devices
- Safety

Early Raman instrument



Modern Raman instrument

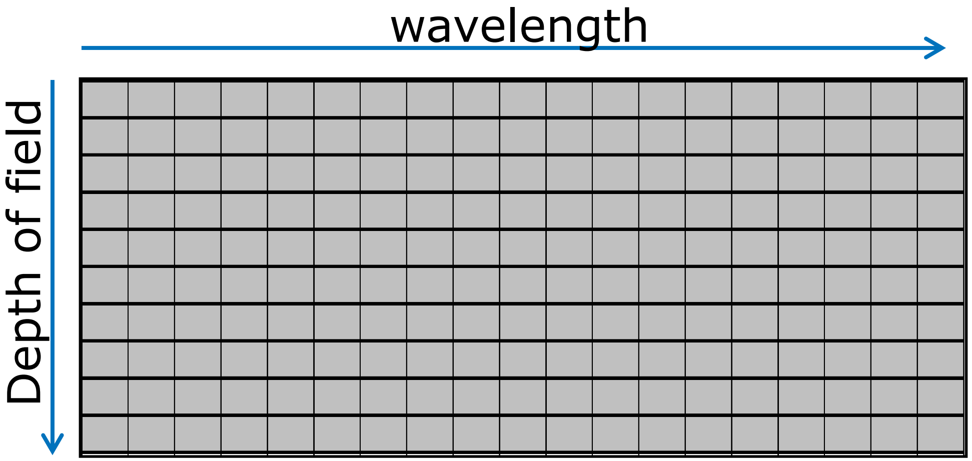


CCD detector impact

- Signal is dispersed along x-axis of detector by grating
- Slit and pinhole define depth of field

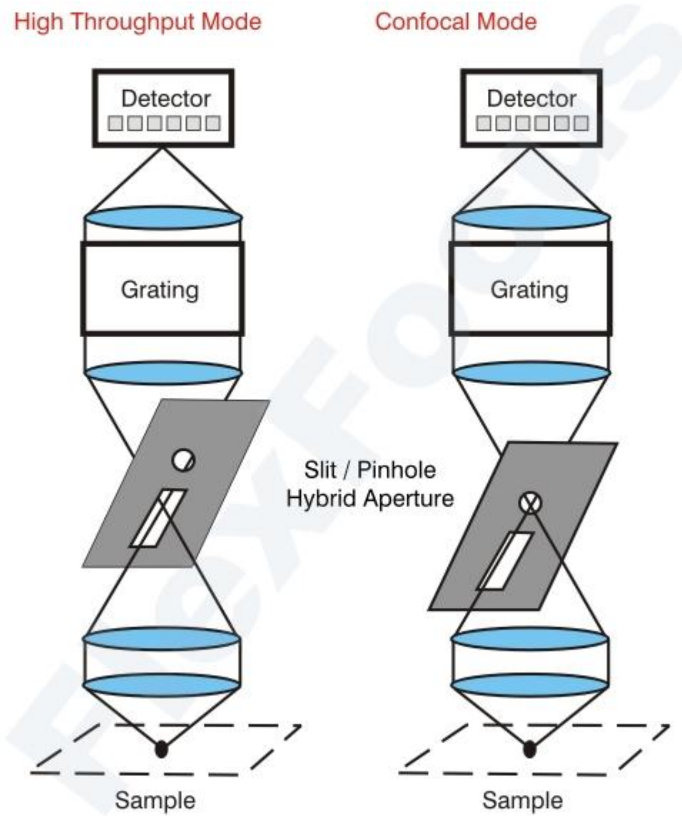
Results

- Improved signal-to-noise
- Much faster
- Frequently better spectral resolution
- Confocal capabilities with pinhole



The array detector

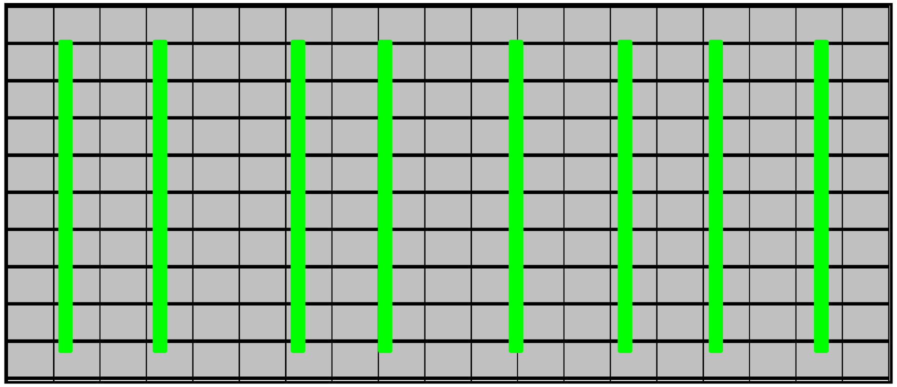
Entrance slits and pinholes



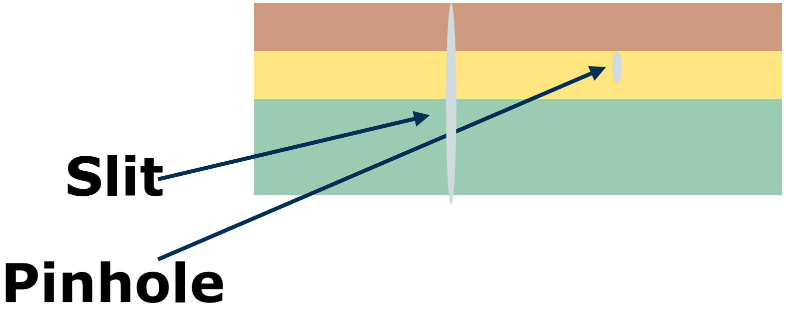
1. Switching between high throughput and high confocal modes of acquisition
2. Depth resolution

Confocal Raman – How does it work?

Array detector



Depth of field in viewing multilayer sample



1. The slide containing the pinholes and slits is projected onto the y-direction of the detector array.

2. With a slit selected, more pixels are illuminated on the detector yielding excellent signal to noise.

3. With a pinhole selected, only light from the depth of interest illuminates the detector.

The detector revisited

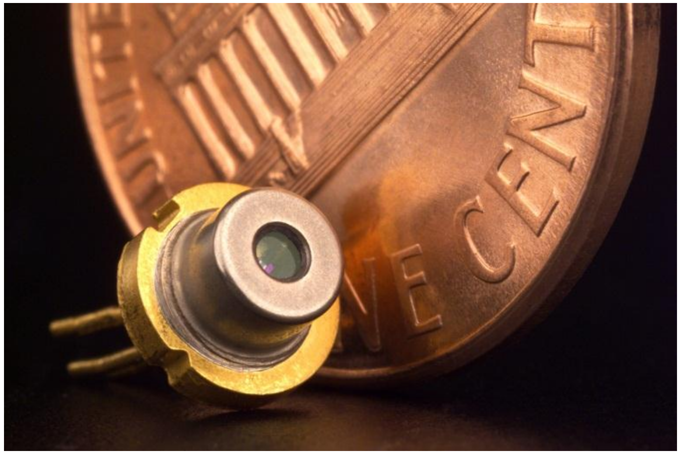
- Detectors in the **visible** are **shot noise limited** and detectors in the **NIR/MIR** are **fixed noise devices**.
- FT/Raman utilizes 1064nm excitation in the NIR with either **InGaAs** or **Ge** detectors. These detectors benefit from using an interferometer to multiplex the light. The improvement can be as much as 50x!

Laser sources

Modern Raman systems use predominantly single frequency diode lasers.

- Inexpensive
- Long lived and reliable
- No water cooling
- Small – easier to employ more than one laser

- Commonly used diode lasers include: **488, 532, 633, 785**, and **830** nm wavelengths.



Non-routine lasers

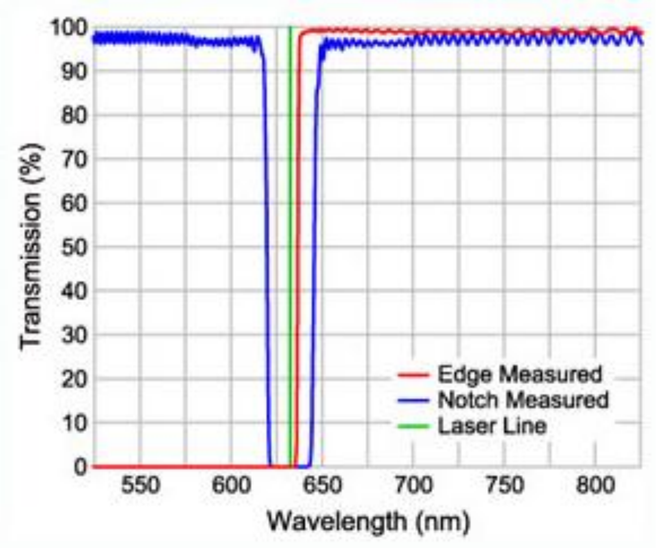
UV lasers

- Expensive
- Short life expectancy

Laser line filters

High optical density filters are used to remove the excitation laser signal

- **Notch filters** – inexpensive option with stoke and anti-stokes preserved.
- **Holographic notch filters** – more expensive option with stokes and anti-stokes preserved and gets to ~100 cm^{-1} of Rayleigh line, do wear out over time
- **Dielectric edge filters** – inexpensive option that gets very close to Rayleigh line but is typically stokes only (~50 cm^{-1})



Power attenuation

- Neutral density filters are frequently employed as diode lasers do not function reliably at partial power

- Having enough power is almost never an issue

- Many samples are sensitive to laser illumination (heating, photo-bleaching, etc.)

- 0.1% laser power is desirable for starting point

Objectives

Objectives have several parameters of interest

- Magnification
- Numerical aperture (NA)
- Working distance
- Air or immersion operation
- Modes of use - brightfield, polarized light, phase contrast, darkfield
- Energy throughput curve

Objective selection and use

Most important factors

- NA is directly related to collection efficiency. The Raman signal will be strongest with high NA objectives. Usually, the higher the NA the smaller the working distance. High NA long working distance objectives are easiest to work with, but can be expensive.
- Fluorite objectives are best for fluorescence illumination and Raman experiments.
- IR shifted objectives work best for excitation wavelengths above 785nm.
- Immersion objectives have the highest NA's

Spatial resolution = $0.61\lambda/NA$

Depth of field = $1.4\lambda/NA^2$

Raman gratings

- Modern Raman systems usually incorporate low and high resolution gratings
- Low resolution gratings provide a larger spectral range, but limited spectral resolution
- High resolution grating acquisitions of the full range are typically the summation of 2-3 high resolution acquisitions stitched together

Note: the spectral range varies as a function of wavelength

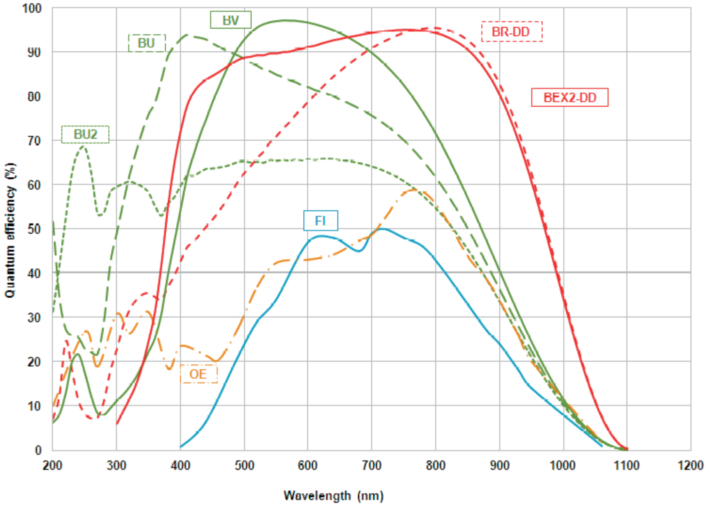
Detectors

- **Single element** – inexpensive and commonly used
- **CCD array cameras** (wavelength is dispersed along x-axis of detector), readout in ms
- **EM-CCD array cameras** (more expensive than “standard” CCD cameras) readout in µs.

Detectors for Raman spectroscopy

- 1024 x 255 high speed spectroscopy multi-channel CCD camera. Back illuminated low noise sensor provides optimized performance from UV through Visible to NIR.

- **Detectors are intended to provide multi-excitation Raman detection**



Typical CCD detector specifications (Andor)

Specifications Summary

- Active pixels 1024 x 255 (1024 x 256 for Bx-DD model)
- Pixel size (W x H) 26 x 26 µm
- Image area 26.6 x 6.6 mm
- Register well depth (typical) 1,000,000 e-
- Maximum TE cooling -100^{o}C
- Maximum spectra per sec 88
- Read noise as low as 4 e-
- Dark current as low as 0.0005 e-/pixel/sec

Why calibrations?

- Anchoring the wavelength and spectral response is important for averaging on data acquisition, spectral subtractions, library searching, and more.

- Diode lasers typically drift to varying degrees.

- Q - How good does a calibration need to be?

- A – Raman data should be wavelength accurate to good as possible (0.3 cm^{-1}).

Calibration Methods and Standards

- The ASTM has adopted 8 standards for the wavelength calibration (ASTM E 1840).

  1. naphthalene (Mallinckodt #94848)
  2. 1,4 bis (2-methylstyryl) benzene (BMB) (Aldrich #25,740-0)
  3. sulfur (Aldrich #41,498-0)
  4. 50/50 (v/v) toluene/acetonitrile (Mallinckrodt Analytical Reagents)
  5. 4-acetamidophenol (active ingredients of Tylenol) (Aldrich A730-2)
  6. benzonitrile (Baker B883-07)
  7. cyclohexane (Mallinckrodt Analytical Reagents)
  8. polystyrene (Aldrich #18,243-5)

Calibration Methods and Standards

- Intensity correction can be accomplishes by white light or glass. Other wavelength corrections are in ASTM committee.
- NIST SRM 2241 - Relative Intensity Correction Standard for Raman Spectroscopy: 785 nm Excitation

Video cameras

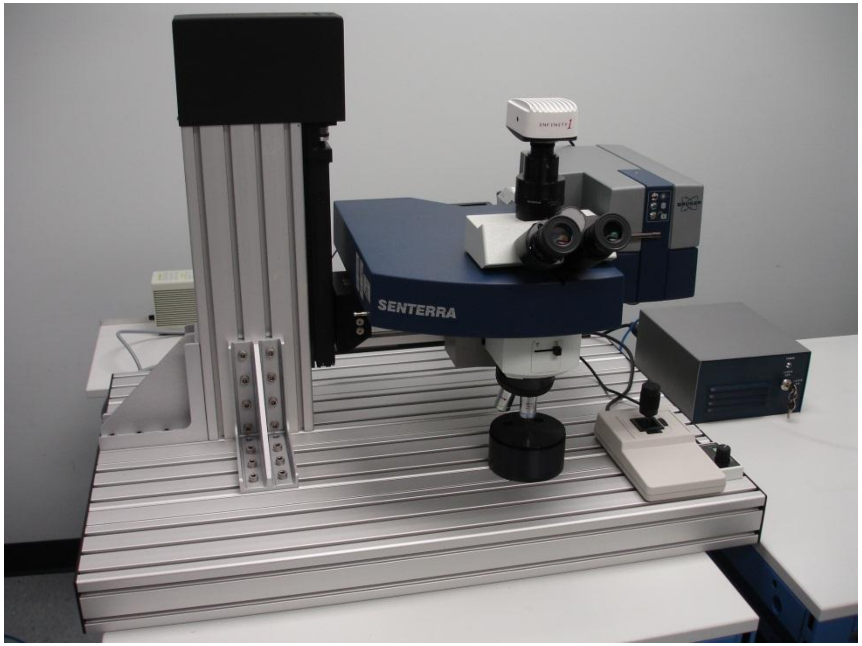
Factors to consider for video cameras

1. Color accuracy
2. Pixel density
3. Low light sensitivity
4. Auto-exposure capabilities
5. Cost

Microscope stages

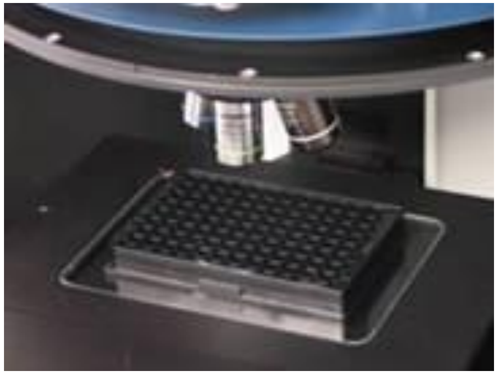
The are a variety of microscope stages available. Select the best one for range of samples you expect to analyze.

- Manual and glide stages – Easy to use and inexpensive
- Motorized stages – Can be expensive for good quality
    - Look for at least ~2x better than what you need
    - Look for accuracy and speed
    - Integration into software for arraying data collection
    - Should have a flat surface and be able to hold most any insert, such as a heating unit
- Z-stage – Great for large samples and still use a motorized stage
- Z-focus – Must be safe for art!

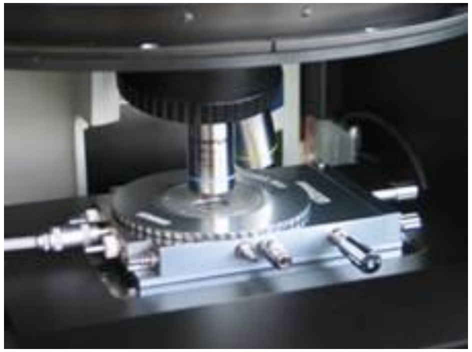


Useful microscope stage based accessories

Multi-position well plates (96 or 384)



Temperature and humidity controlled cells



Right turn objective elbows

Probes

- There are many manufactures offering probes. Probes must include additional laser and Raman filters. The laser light passes down the fiber generating a Raman signal of the fiber, so a band pass filter must be employed to remove the Raman signal. After impinging on the sample, the laser is filtered to prevent the generation of a signal from the fiber.

- Rugged probes, viewing probes, etc. are available. Almost any configuration can be customer made (for a price).

Handheld devices

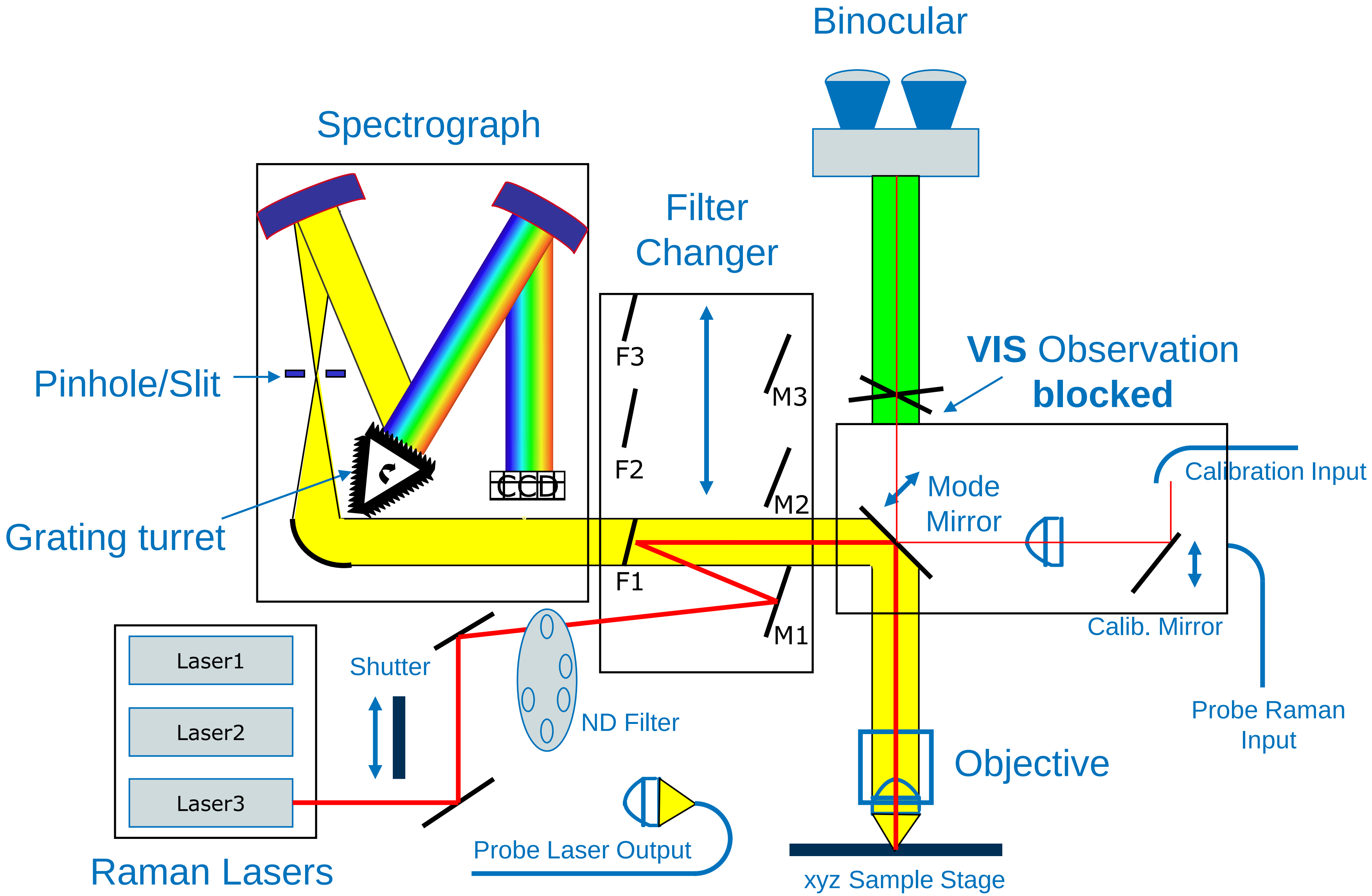
- Handheld devices are essentially miniature Raman systems using the same components as larger units.
- Typically, some sacrifices are made with respect to performance to meet the demands of portability.
- However, as innovations in component technology results in smaller units with good performance, portable units will be used regularly in the near future.

Safety

- Raman systems employ Class 3B and 4 lasers that present significant safety risks, if handled improperly.
- Modern Raman microscope systems are Class I laser safe products with safety enclosures.
- Z-stage microscope, handheld, and probe based Raman systems are Class 3B or 4 systems that require care for safe operation.

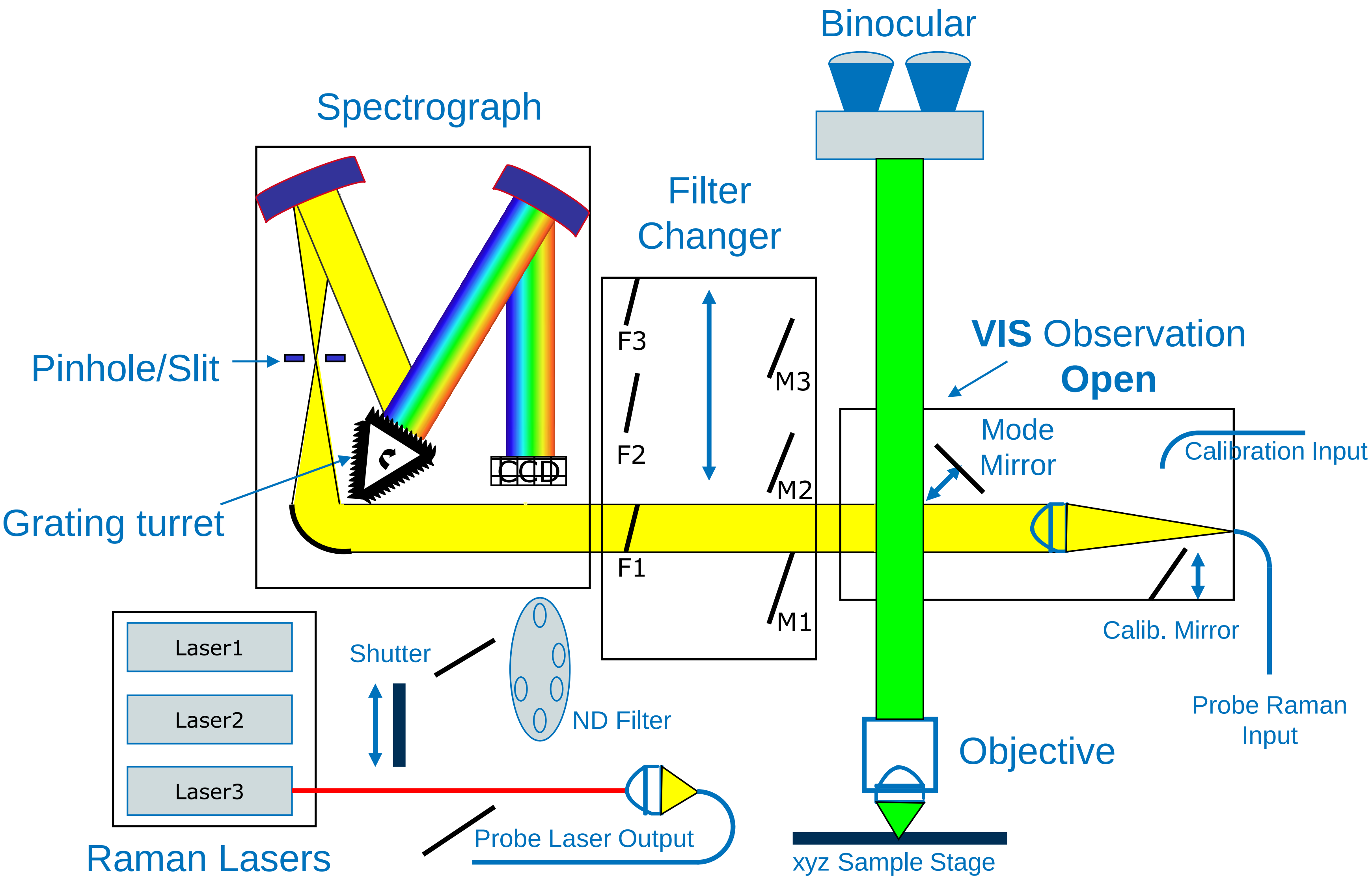
Putting it all together

Modern Raman Microscope

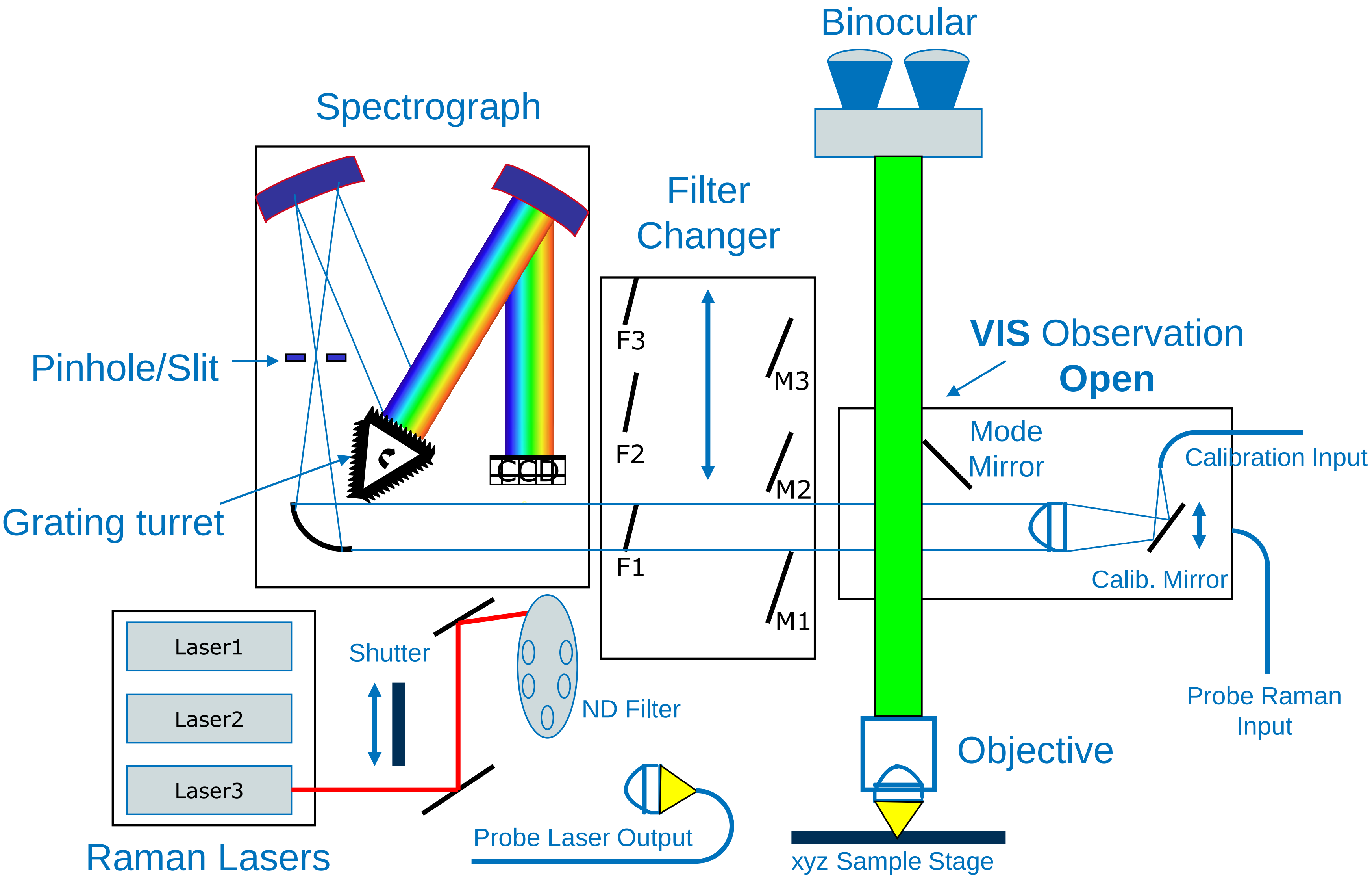


Bruker Optics

Raman Probe Configuration



Calibration Mode



Summary

- Key components of Raman instrumentation have been improved significantly through coincidental breakthroughs in related industries (see telecom rise and fall) as well as the efforts of researchers focused on improving Raman analysis capabilities.

- Today's systems are robust, well calibrated, less expensive, easy-to-use, and capable of high performance data collection. Improvements in software make data collection, manipulation, and evaluation much easier than in the past. This is particularly true for image processing.

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman analysis of minerals & pigments

Richard Newman

Museum of Fine Arts, Boston, US

THURSDAY, SEPTEMBER 27: LECTURE 4

Raman analysis of minerals & pigments

Richard Newman

Scientific Research Lab
Museum of Fine Arts, Boston

Outline

1. Raman vs. IR spectroscopy for inorganics: a quick comparison

2. "Group frequencies" for trigonal (carbonate) and tetrahedral (sulfate, phosphate, chromate, arsenate) polyatomic anions

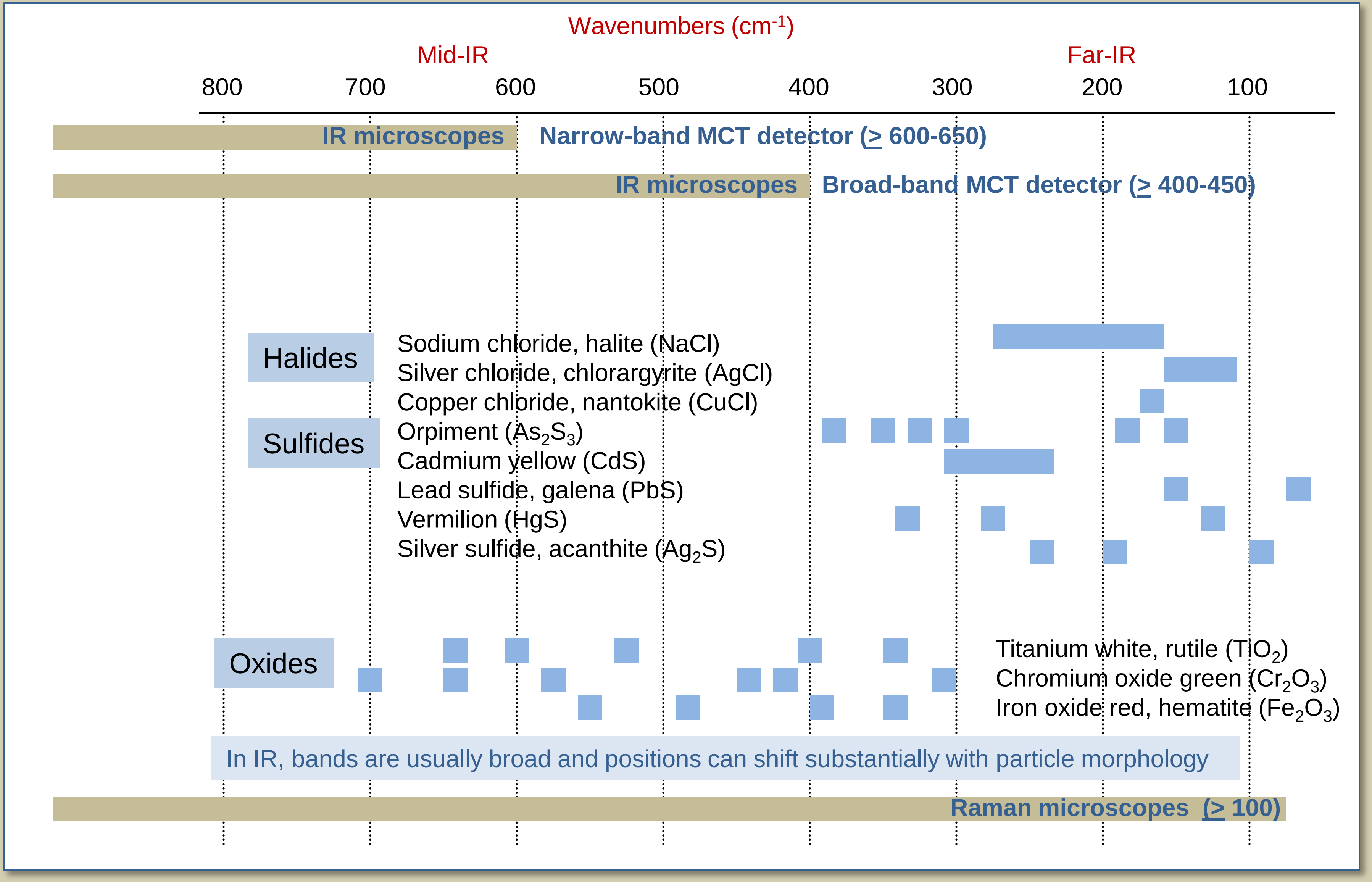
   a. internal vs. external vibrations: common features; what to look for to distinguish between different compounds containing the same anion
   b. distinguishing solid solutions
   c. effect of very small particle sizes
   d. hydroxyl groups and water

3. Silicates: a special type of polyatomic ion

   a. compounds with isolated silicon tetrahedra
   b. other silicates
   c. crystalline vs. glassy silicates

1. Raman vs. IR spectroscopy for inorganics: a quick comparison

Characteristic vibrational frequencies for halide salts, sulfides and anhydrous oxides



IR microscopes Narrow-band MCT detector (≥ 600-650)

IR microscopes Broad-band MCT detector (≥ 400-450)

Halides

Sulfides

Sodium chloride, halite (NaCl)
Silver chloride, chlorargyrite (AgCl)
Copper chloride, nantokite (CuCl)
Orpiment (As_2S_3)
Cadmium yellow (CdS)
Lead sulfide, galena (PbS)
Vermilion (HgS)
Silver sulfide, acanthite (Ag_2S)

Oxides

Titanium white, rutile (TiO_2)
Chromium oxide green (Cr_2O_3)
Iron oxide red, hematite (Fe_2O_3)

In IR, bands are usually broad and positions can shift substantially with particle morphology

Raman microscopes (≥ 100)

Instrumentation used for spectra in this presentation

Thermo Nicolet iS10 FTIR spectrometer with Continuum IR microscope, narrow band MCT detector (> 650 cm^{-1})

- Samples pressed on a diamond window and analyzed by transmittance
- Resolution 4 cm^{-1}
- No corrections to data

Bruker SENTERRA dispersive Raman microscope with 532, 633 and 785 nm lasers

- Resolution ~ 3-5 cm^{-1}
- Analyses usually carried out only over lower wavenumber range
- No polarization
- Calibration > 0.1 cm^{-1} (carried out simultaneously with data acquisition)
- Usually no corrections to data; sometimes background correction or smoothing as indicated

Comments:

- Shorter wavelength laser (blue) is best for glass
- Because of fluorescence, FT-Raman may work for some minerals when dispersive Raman does not

2. “Group frequencies” for trigonal (carbonate) and tetrahedral (sulfate, phosphate, chromate, arsenate) polyatomic anions

Bonding within the anion (covalent) is much stronger than bonding between anion and cation (ionic)

Most can be characterized by both IR and Raman

Vibrational spectra of compounds containing polyatomic ions

External vibrations

Internal vibrations of anion

400 cm^{-1} and below
accessible with Raman
only

400-1200 cm^{-1}
accessible with Raman, at least
some in IR

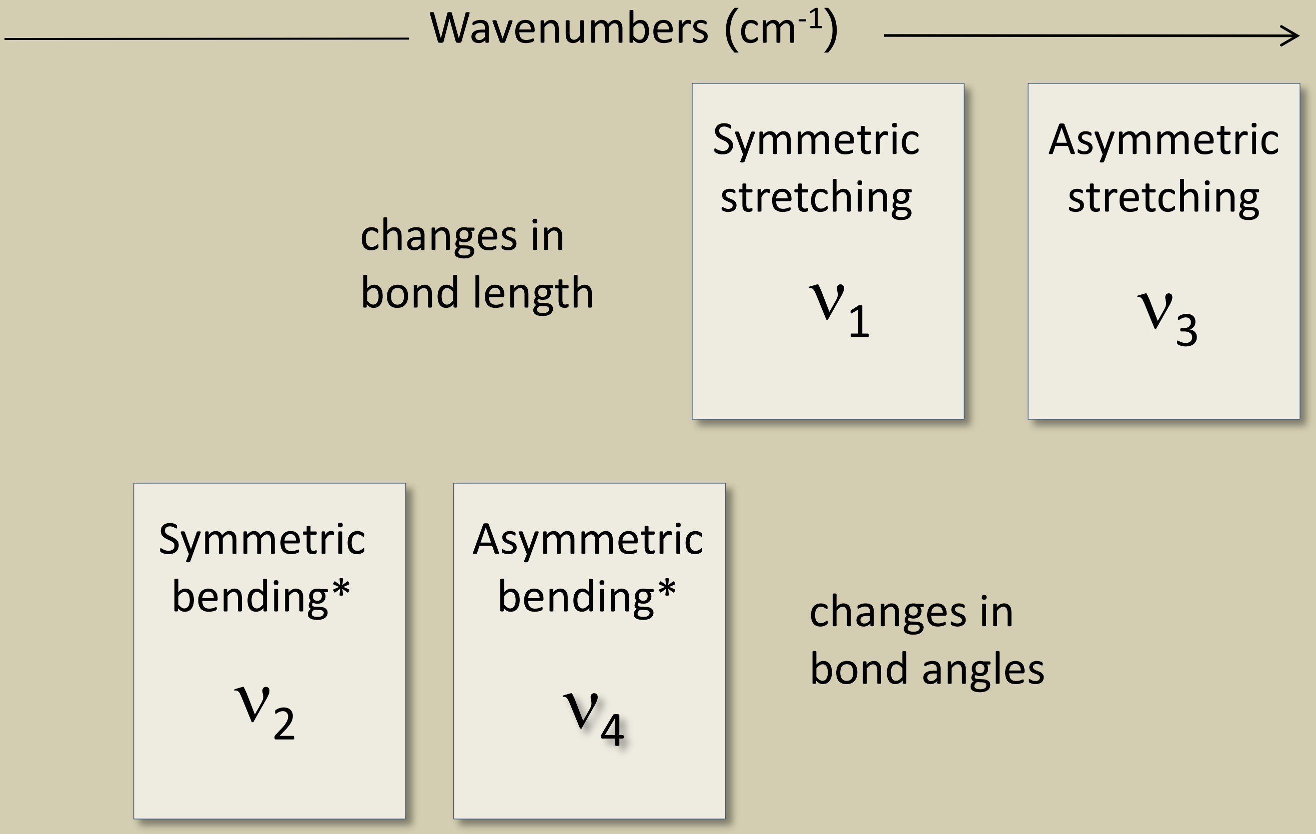
Wavenumbers (cm^{-1}) →

Translations and rotations of cations and anions

Bending and stretching of covalent bonds within the anion

If water or OH$^-$ is present, bands at higher frequencies also will be present (IR, usually less satisfactorily in Raman)

Internal vibrations of anion (typically four modes)



Wavenumbers (cm^{-1})

changes in
bond length

Symmetric
stretching

ν_1

Asymmetric
stretching

ν_3

Symmetric
bending*

ν_2

Asymmetric
bending*

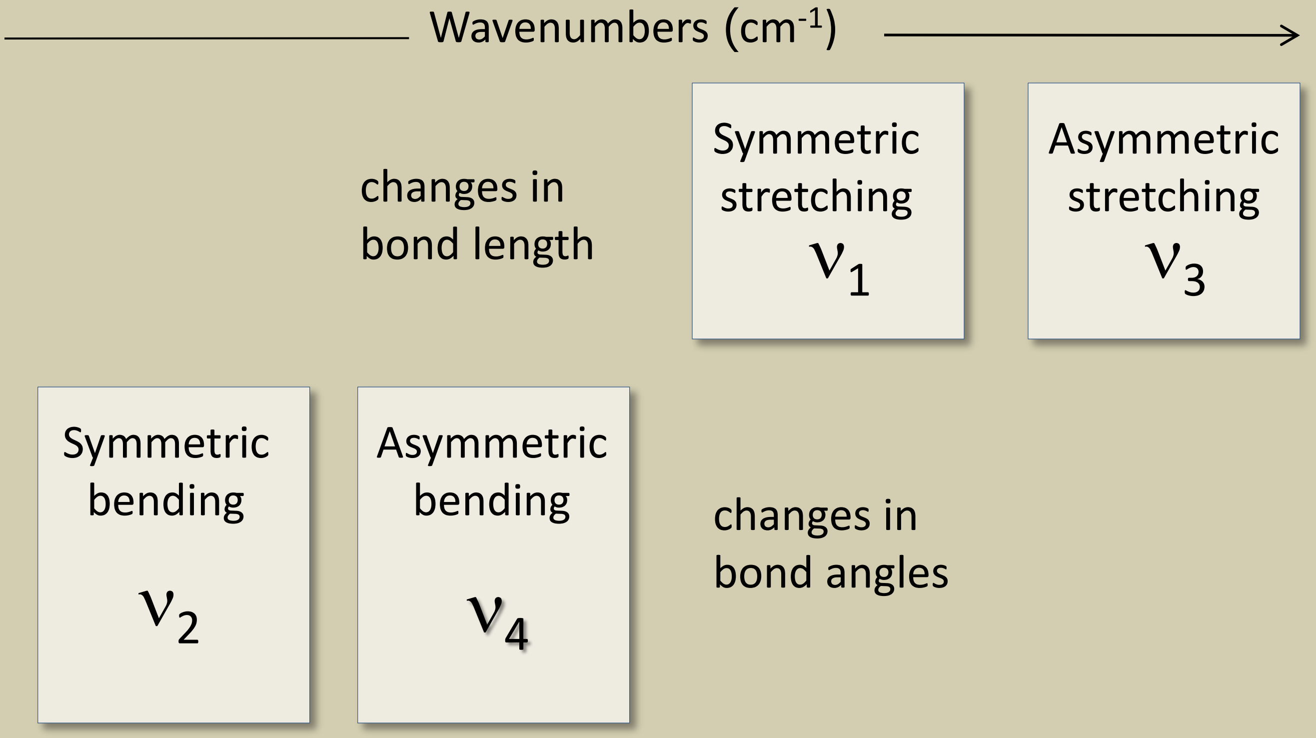
ν_4

changes in
bond angles

Common order of frequencies (but this is not always the case)

* There are different descriptions for trigonal ions (such as carbonate)

Internal vibrations of anion (typically four modes)



Wavenumbers (cm^{-1})

changes in bond length

Symmetric stretching ν_1

Asymmetric stretching ν_3

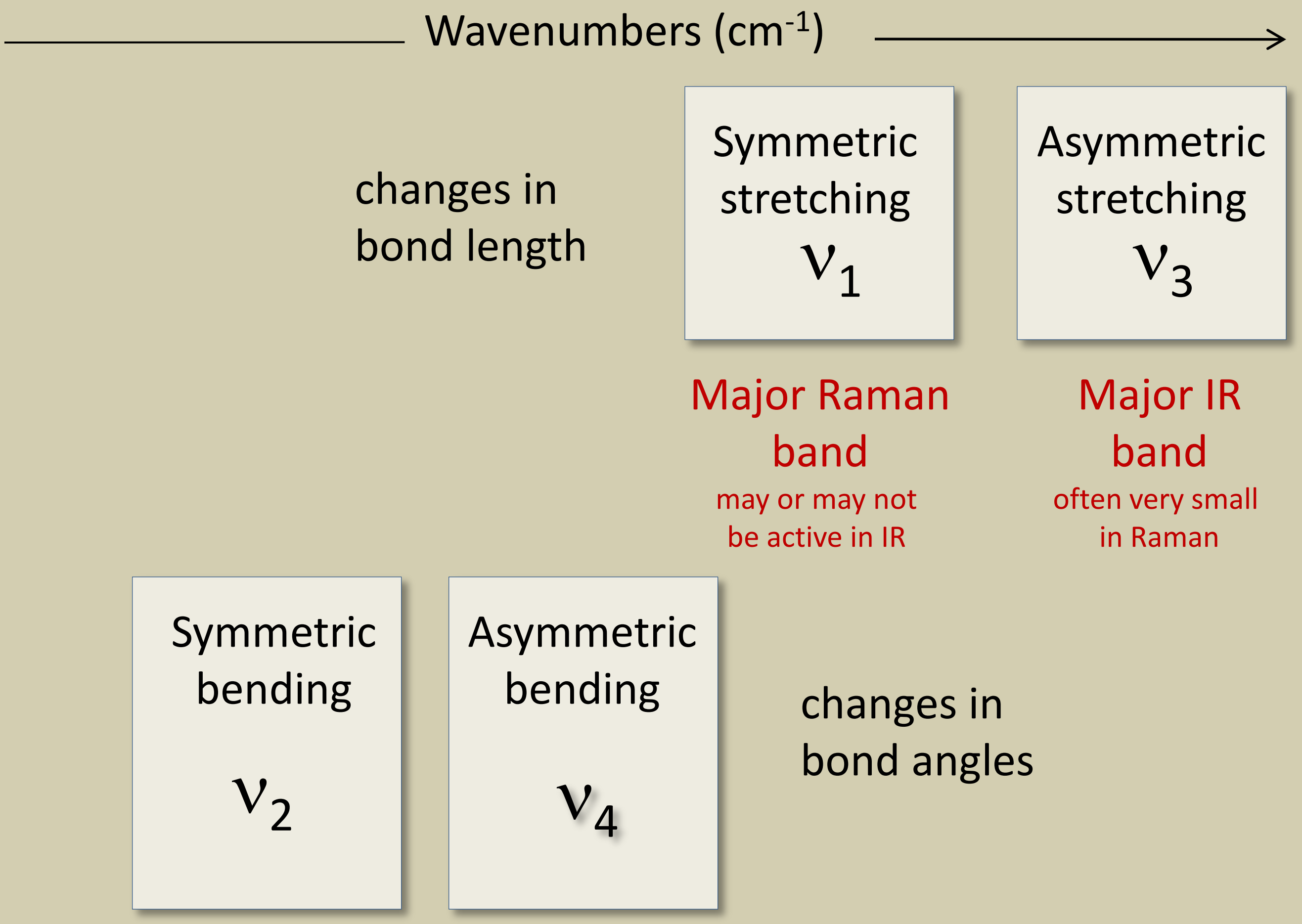
Symmetric bending ν_2

Asymmetric bending ν_4

changes in bond angles

There may be two or three closely spaced peaks for some of these modes in some compounds (doubly and triply degenerate modes)

Internal vibrations of anion (typically four modes)



Wavenumbers (cm^{-1})

changes in
bond length

Symmetric
stretching
ν_1

Asymmetric
stretching
ν_3

Major Raman
band
may or may not
be active in IR

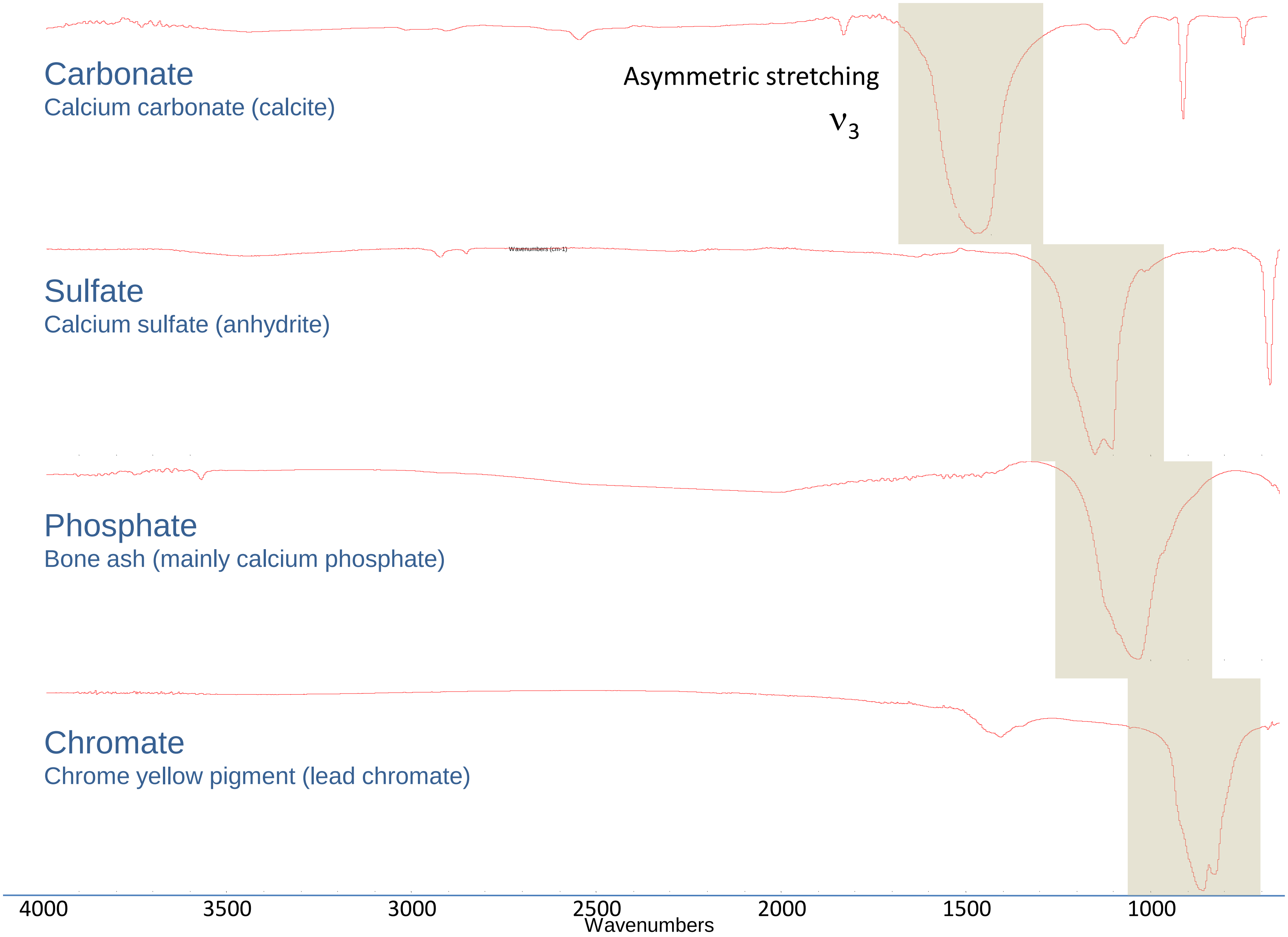
Major IR
band
often very small
in Raman

Symmetric
bending
ν_2

Asymmetric
bending
ν_4

changes in
bond angles

IR spectra of (anhydrous) compounds containing inorganic polyatomic ions



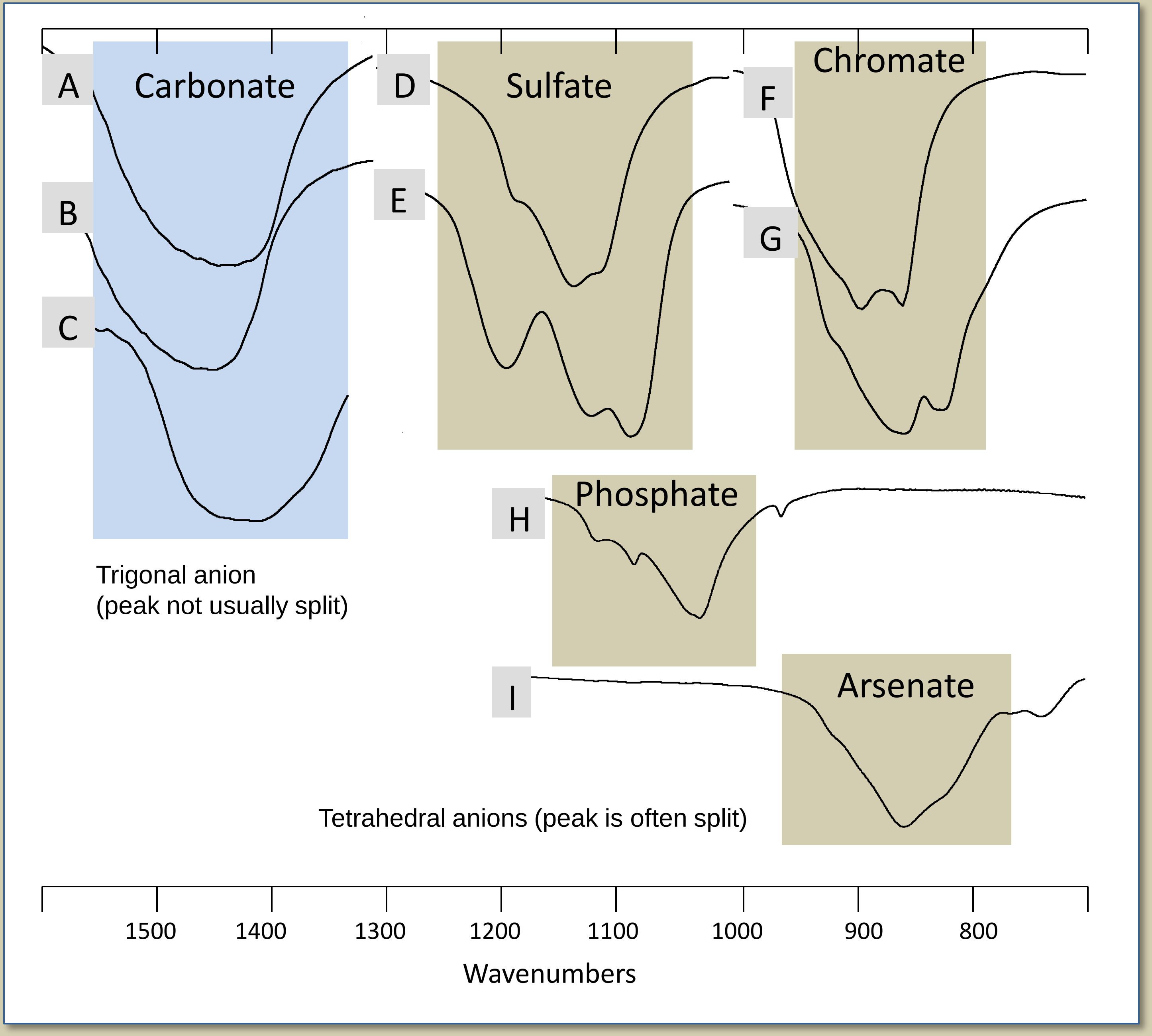
Carbonate
Calcium carbonate (calcite)

Sulfate
Calcium sulfate (anhydrite)

Phosphate
Bone ash (mainly calcium phosphate)

Chromate
Chrome yellow pigment (lead chromate)

Asymmetric stretching vibrations (IR) of various polyatomic ions



A, calcite , CaCO3
B, dolomite, CaMgCO3
C, magnesite, MgCO3

D, gypsum, CaSO4.2H2O
E, barite, BaSO4

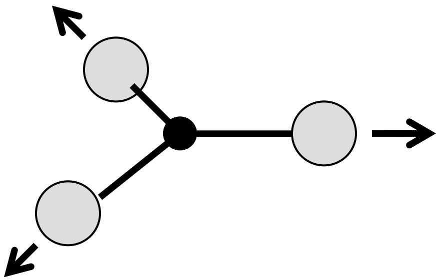
F, strontium chromate yellow, $SrCrO_4$
G, lead chromate yellow, $PbCrO_4$

H, hydroxylapatite, $Ca_3(PO_4)_3(OH)$.

I, cobalt violet, $(Mg,Co)_3(AsO_4)_2$

Vibrations within the isolated carbonate ion

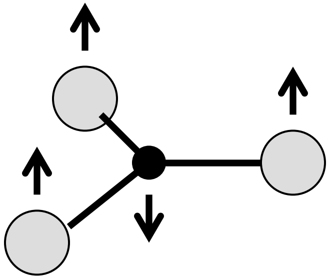
4 modes, 6 total vibrations



ν_1 (symmetric stretch)

Raman active

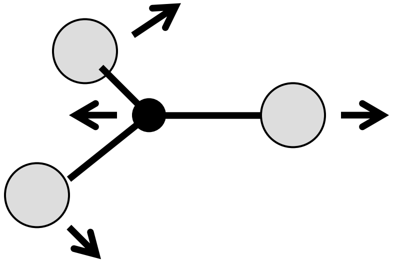
1063 cm^{-1}



ν_2 (out-of-plane bend)

IR active

879 cm^{-1}

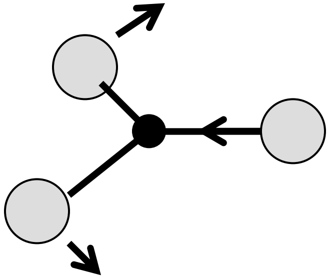


ν_3 (asymmetric stretch)

Doubly degenerate*;

IR and Raman active

1415 cm^{-1}



ν_4 (in-plane bend)

Doubly degenerate*;

IR and Raman active

680 cm^{-1}

* Only one of the degenerate vibrations is shown

Symmetry of the isolated polyatomic ion is usually higher than symmetry of the ion when it is in a crystalline compound

→ in compounds, degenerate bands may be split and inactive bands may appear

→ in compounds, there can be more bands associated with a given vibration than are possible for the isolated polyatomic ion (dependant on chemical composition and crystal structure)

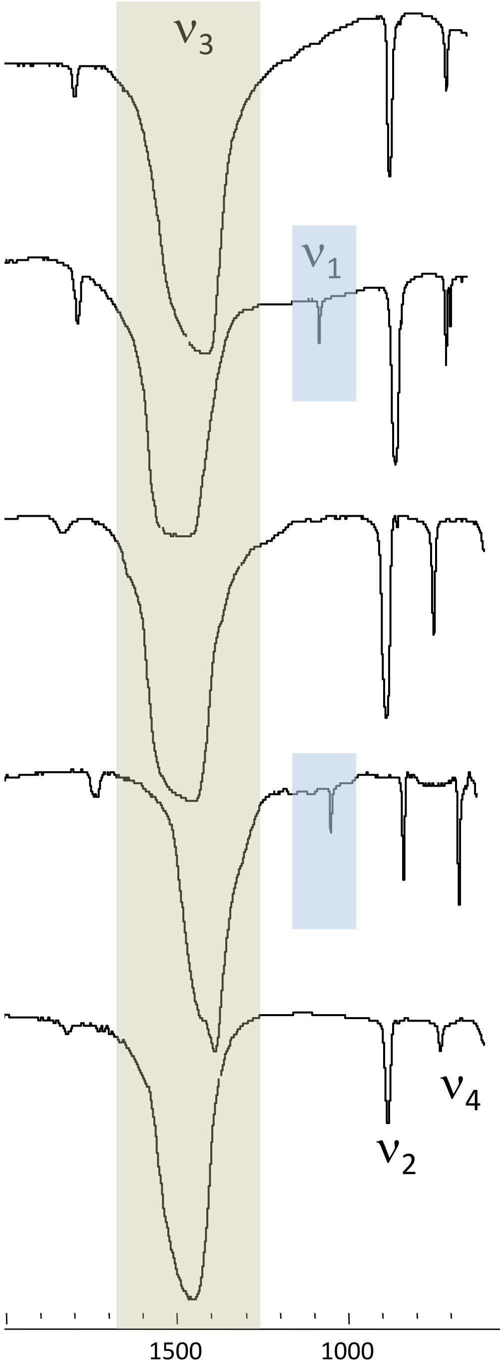
Calcite
$CaCO_3$

Aragonite
$CaCO_3$

Magnesite
$MgCO_3$

Cerussite
$PbCO_3$

Dolomite
$CaMg(CO_3)_2$



IR spectra of some anhydrous carbonates; expected three modes of isolated carbonate ion are present in those in gold boxes

Symmetric stretch, inactive in isolated ion, is active in aragonite and dolomite

All active bands (stretching and bending) are within mid-IR range (>600 cm^{-1})

Movements of atoms during vibrations can be described by symmetry operations involved in the movements (group theory), which give different symmetry species

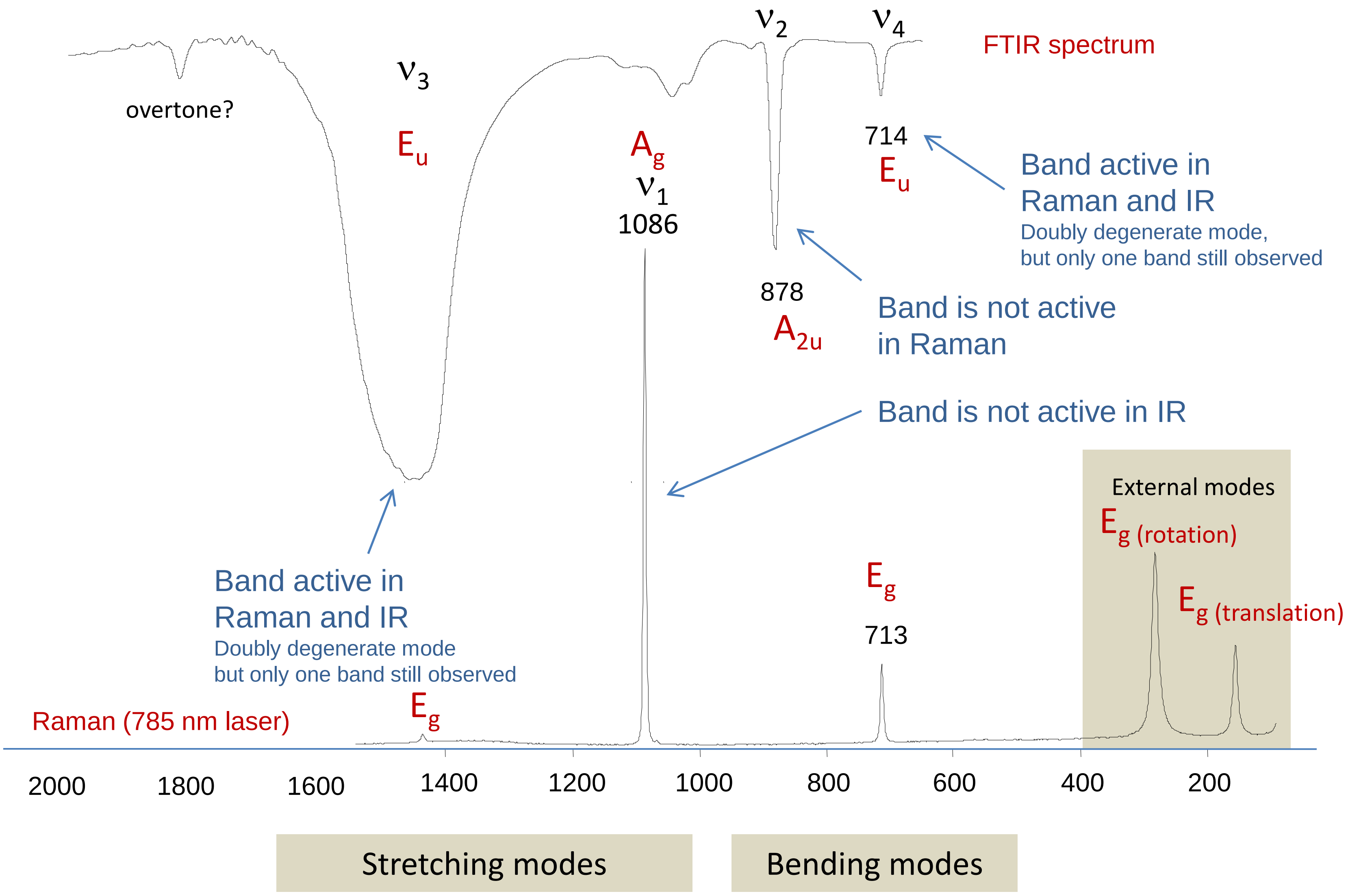
“One dimensional” (unique vibrations) ⟶ A and B

“Two dimensional” (doubly degenerate vibrations) ⟶ E

“Three dimensional” (triply degenerate vibrations) ⟶ T (or F)

Each vibrational band in an IR or Raman spectrum can be labeled with one of these designations – there are also subscripts and superscripts that may be present on each, e.g. $A_{1,}$ E_{1g} etc.

A, B, E and T or F are Mulliken notations, which are the ones most commonly used



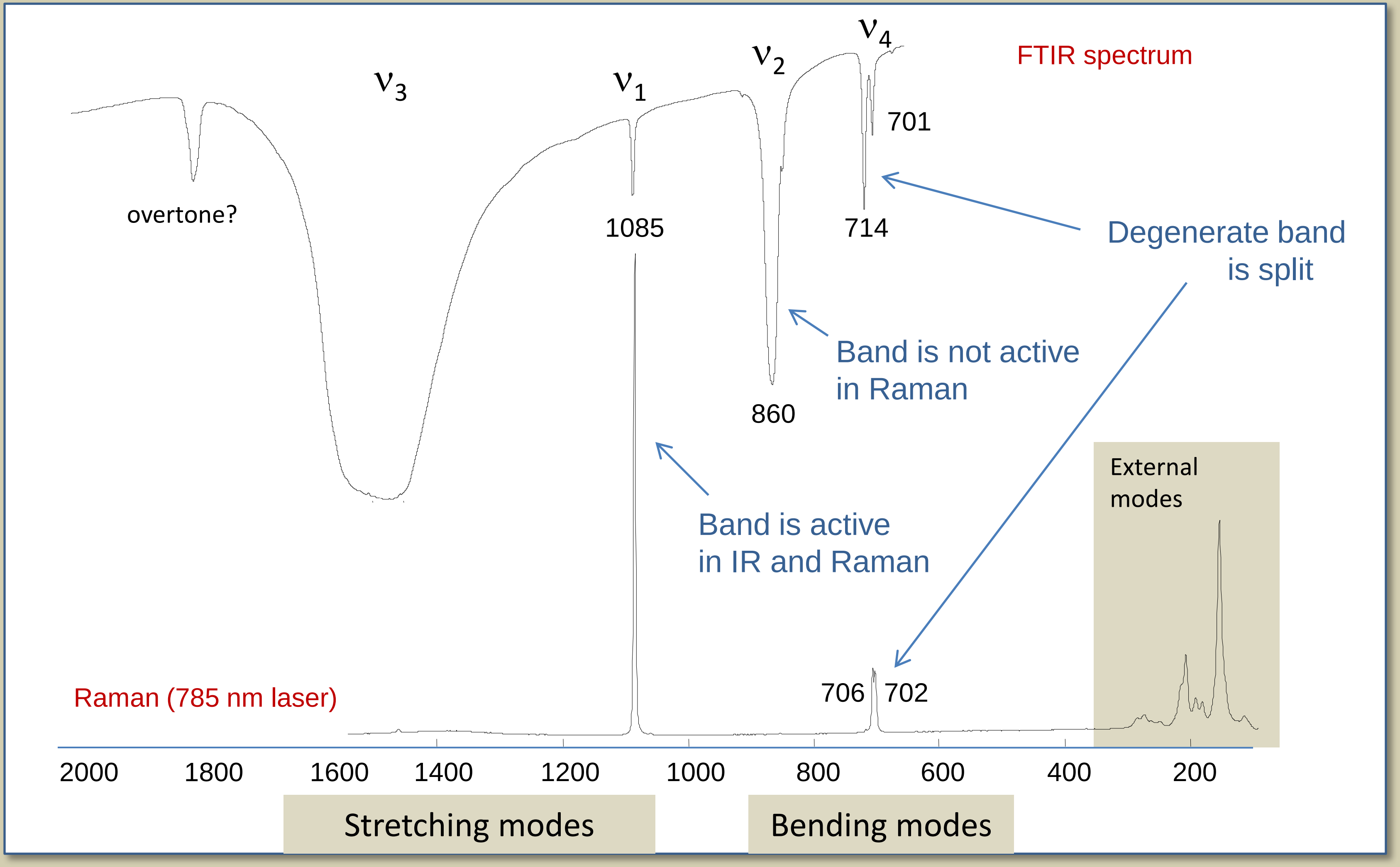
Band active in Raman and IR
Doubly degenerate mode, but only one band still observed

Band is not active in Raman

Band is not active in IR

Band active in Raman and IR
Doubly degenerate mode but only one band still observed

Comparison of IR and Raman spectra of calcite, $CaCO_3$



Degenerate band is split

Band is not active in Raman

Band is active in IR and Raman

Comparison of IR and Raman spectra of aragonite, $CaCO_3$

Some compounds are nearly pure (virtually fixed compositions), but substitution in the cation(s) often occurs

Replacement of end-member cation by small amounts of another cation usually produces little obvious change in internal mode frequencies of polyatomic anion

Example: calcite ($CaCO_3$) may contain some magnesium, up to a few percent, but the presence of such substitution would be virtually impossible to determine by vibrational spectroscopy

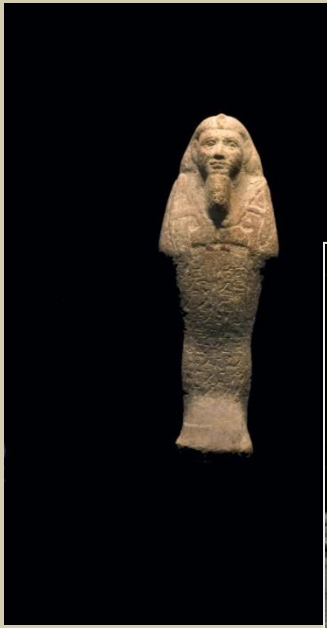
Minor substitution still may show little affect on internal modes – what effects do occur can easily be missed

Substitutions affect external (lattice) vibrations more than internal vibrations – these are the vibrations to carefully examine

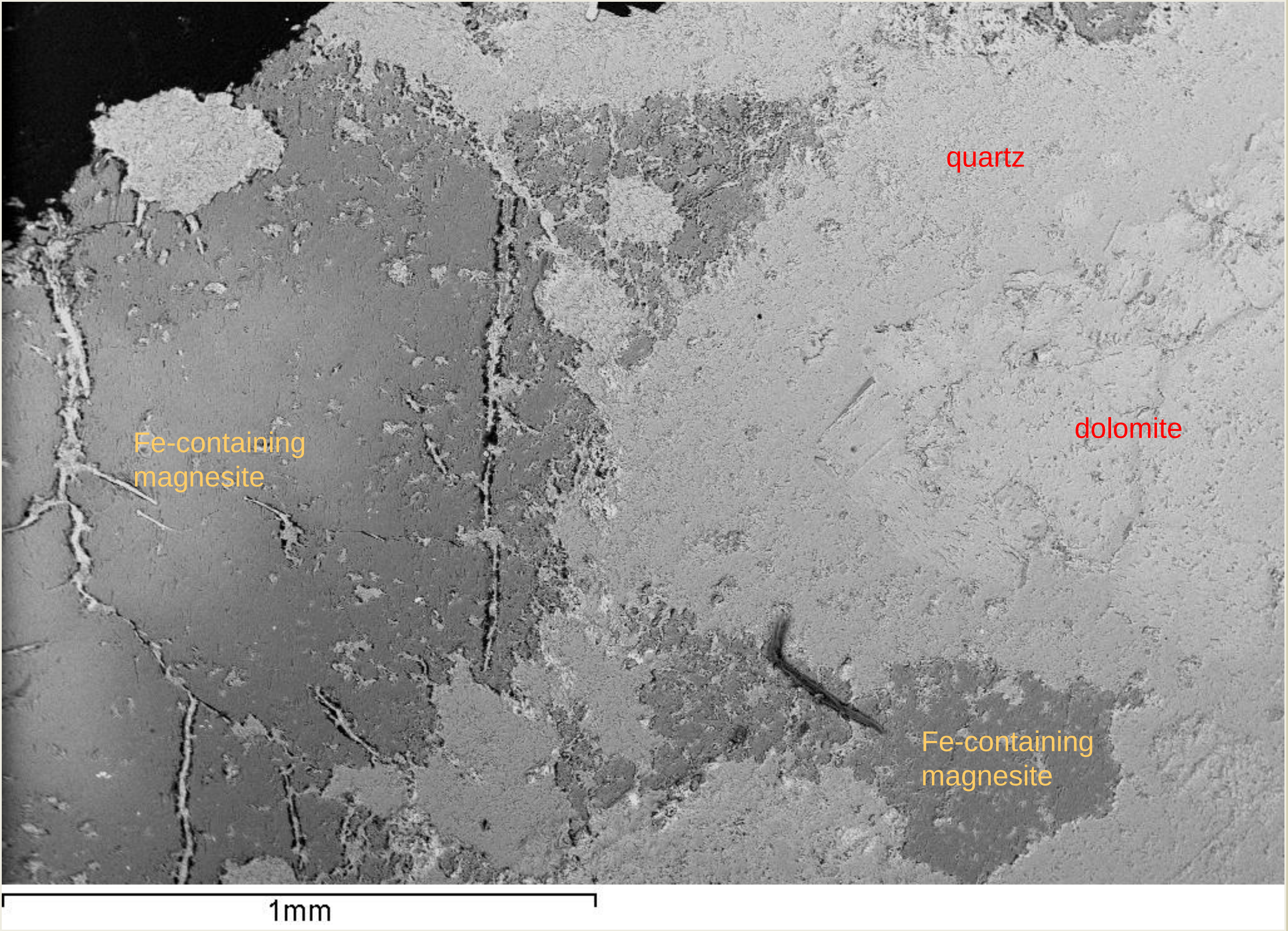
Example: iron substituting for magnesium in magnesium carbonate (magnesite)

Some of the >1,100 stone shawabtys from the pyramid of King Taharqa, Nuri I, Nubia Sudan, 690-884 BC; image adjusted to show original colors of unaltered stones

Left:: Nubian shawabty (MFA 21.15016)



Below: Double-polished thin section of rock from this artifact, back-scattered electron image



Effect of unit cell size (which is directly related to extent of Fe substitution for Mg) on peak position of translation (lattice vibration)

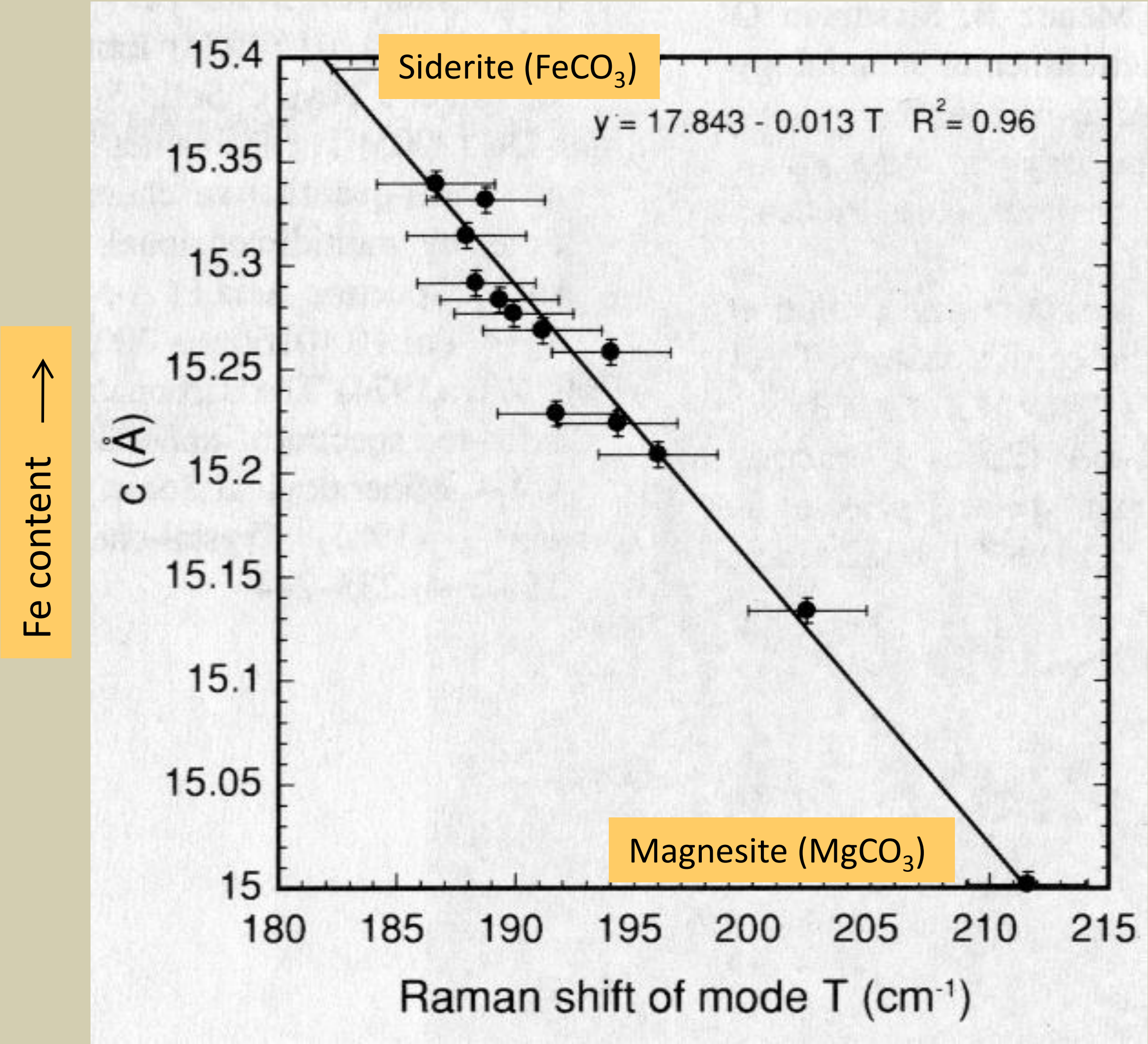
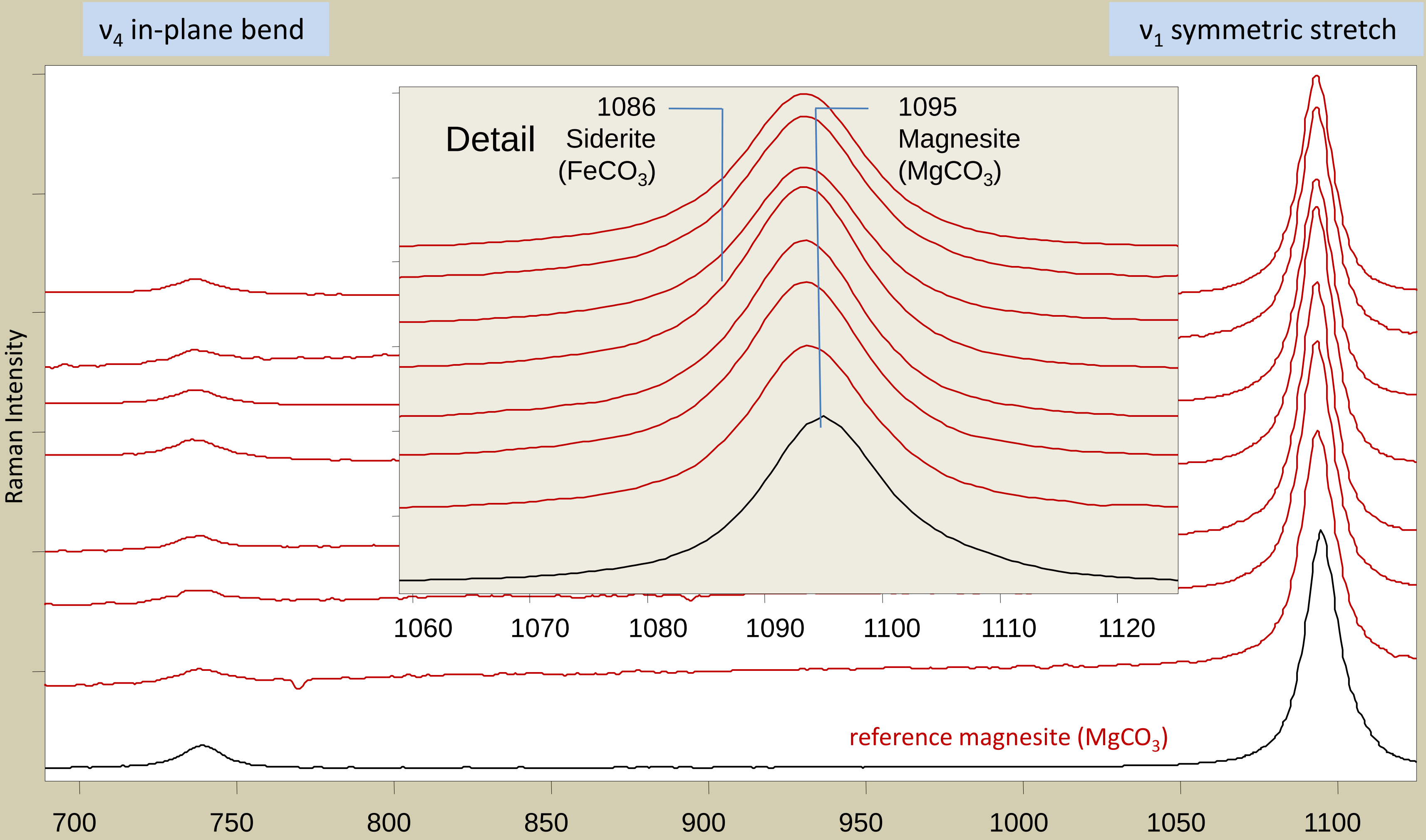


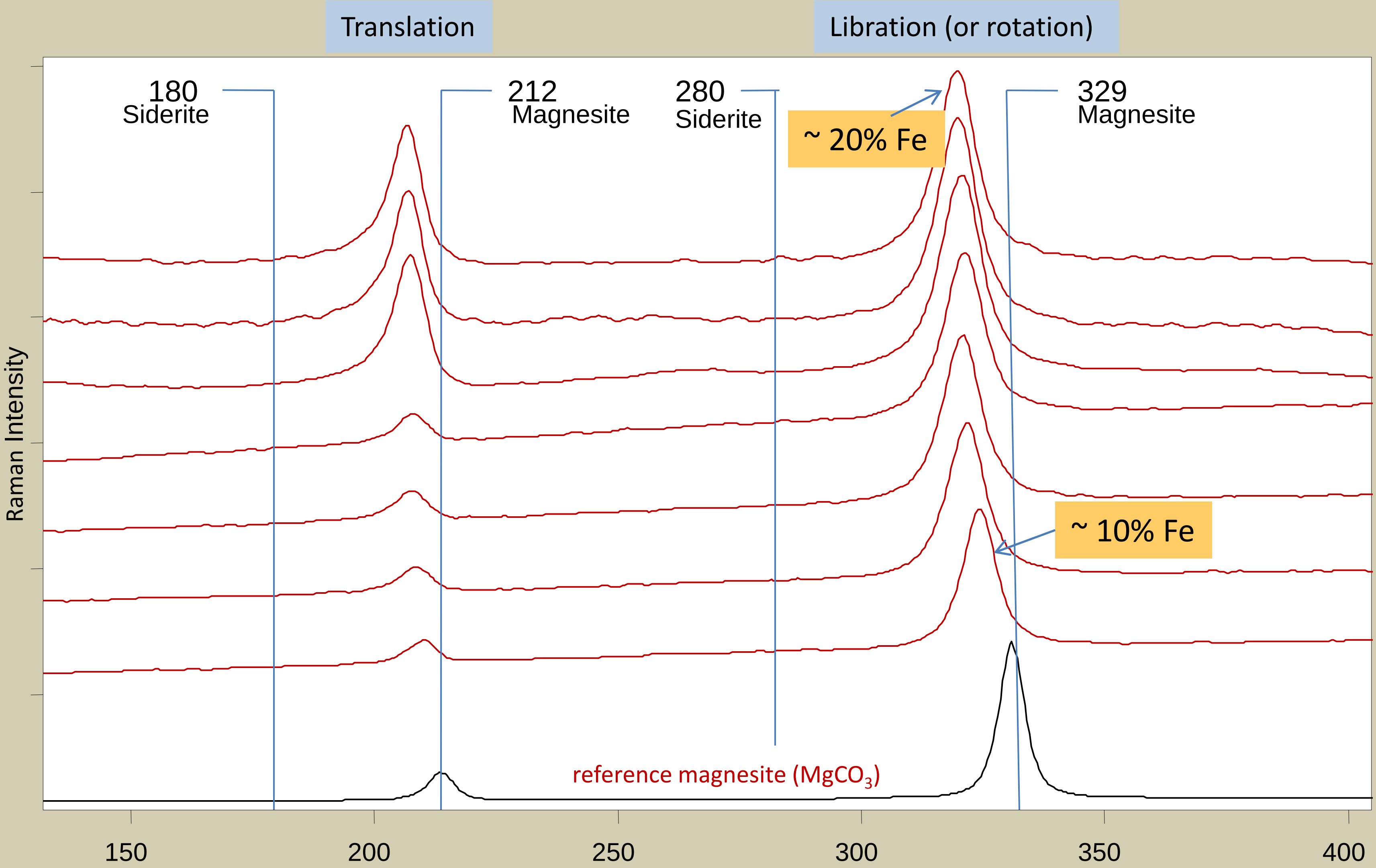
Chart from Boulard et al., *Physics and Chemistry of Minerals* 39 (2012): 239-246



Raman spectra (785 nm laser) of carbonate mineral in thin section from Nubian shawaby

9 cm^{-1} difference between siderite and magnesite

Siderite band positions from Boulard et al., *Physics and Chemistry of Minerals* 39 (2012): 239-246

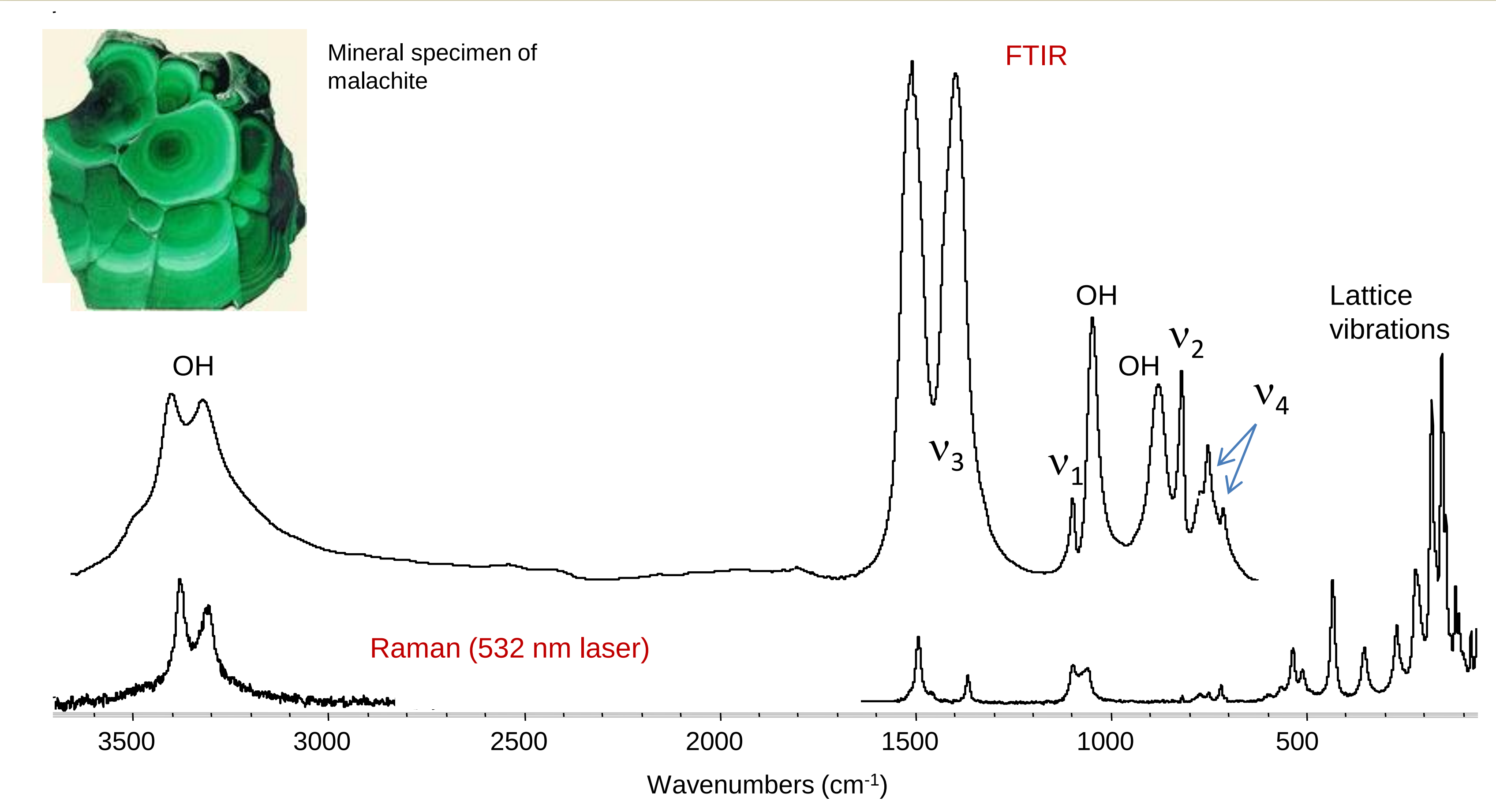


Details of Raman spectra of carbonate mineral in thin section from Nubian shawabty

32 cm^{-1} (T) and 49 cm^{-1} (L) differences between siderite and magnesite

Stretching

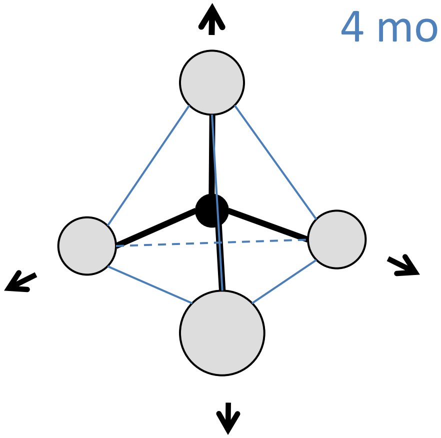
Bending



Comparison of IR and Raman spectra of malachite, $Cu_2(OH)_2CO_3$

Vibrations within the isolated sulfate ion

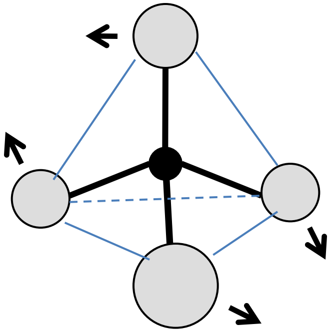
4 modes, 9 total vibrations



ν_1 (symmetric stretch)

Raman active

983 cm-1

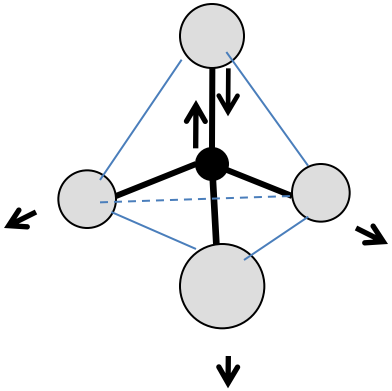


ν_2 (symmetric bend)

Doubly degenerate*;

Raman active

450 cm-1

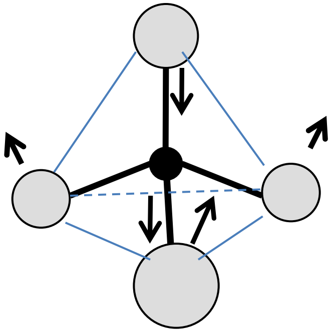


ν_3 (asymmetric stretch)

Triply degenerate*;

IR and Raman active

1106 cm-1



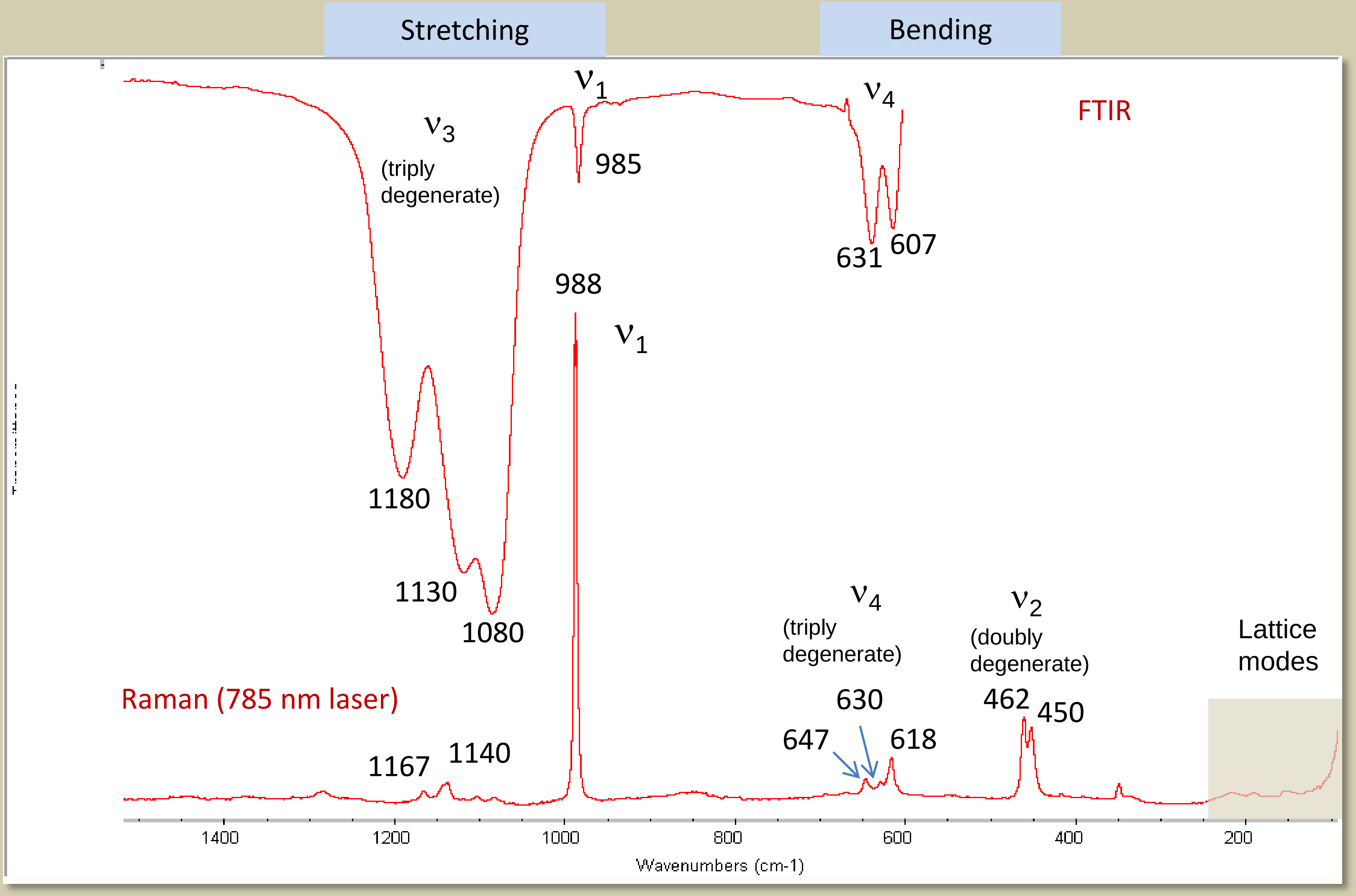
ν_4 (asymmetric bend)

Triply degenerate;*

IR and Raman active

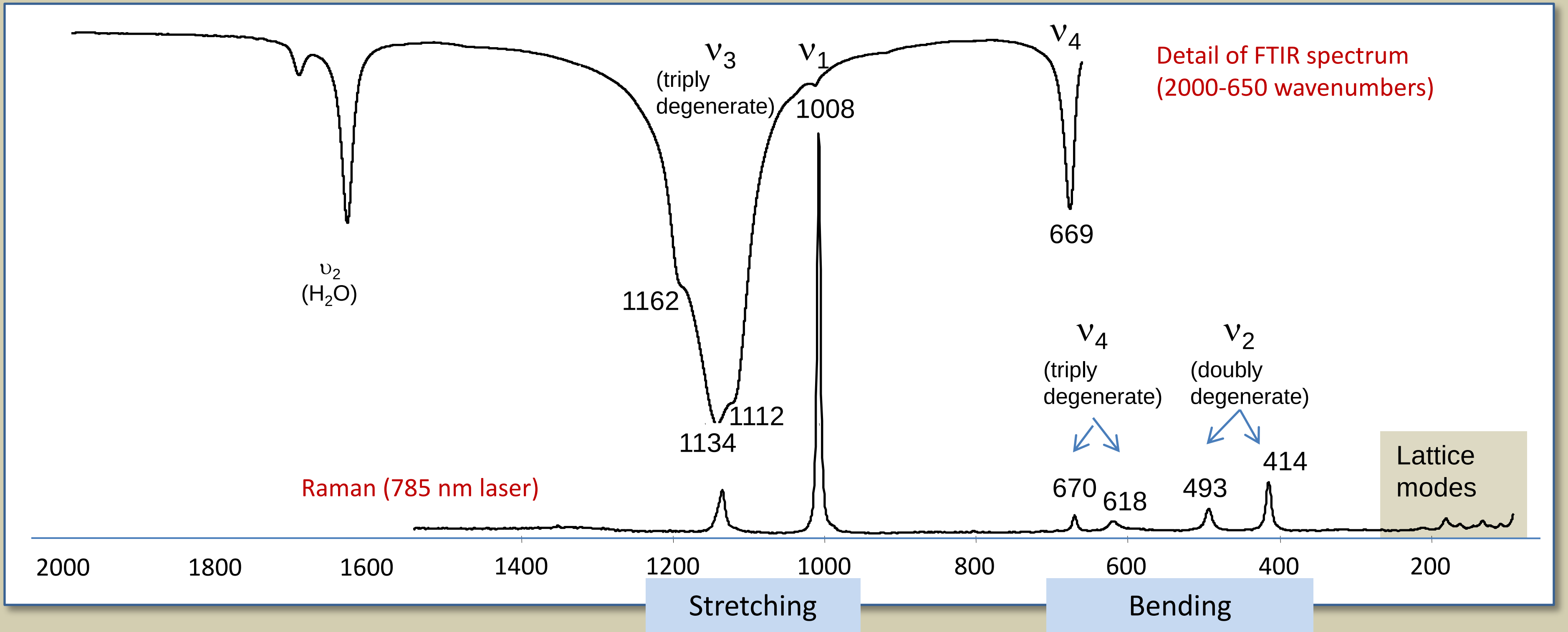
611 cm-1

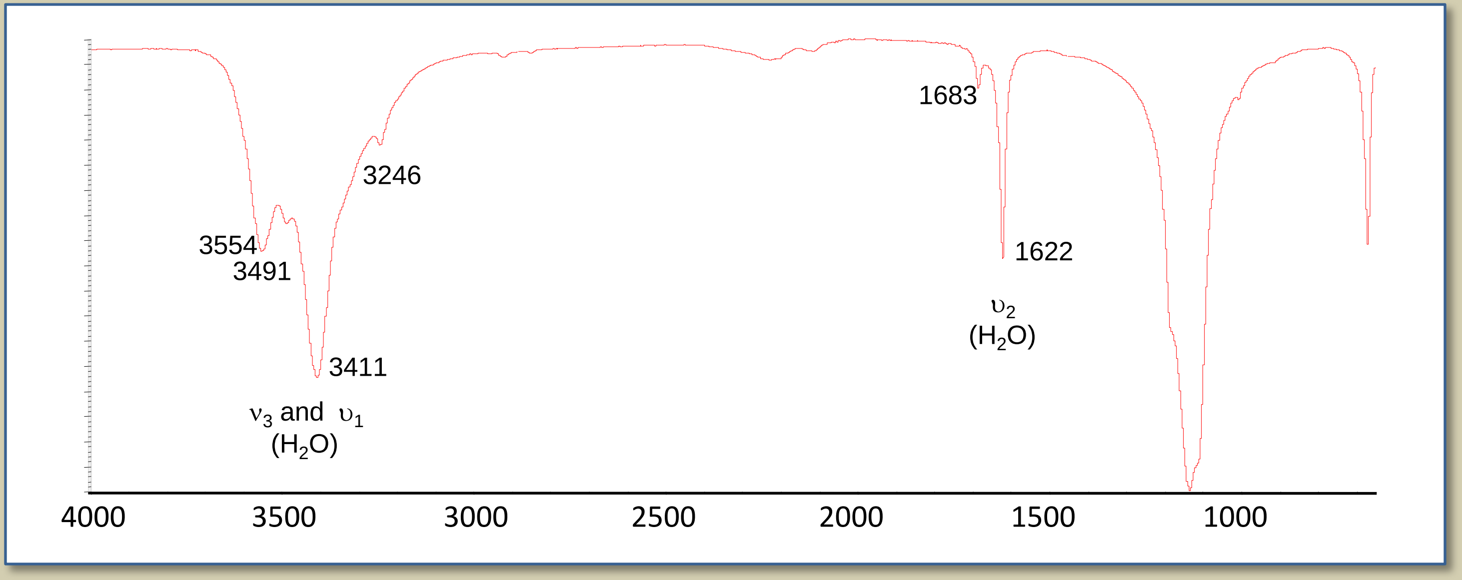
* Only one of the degenerate vibrations is shown



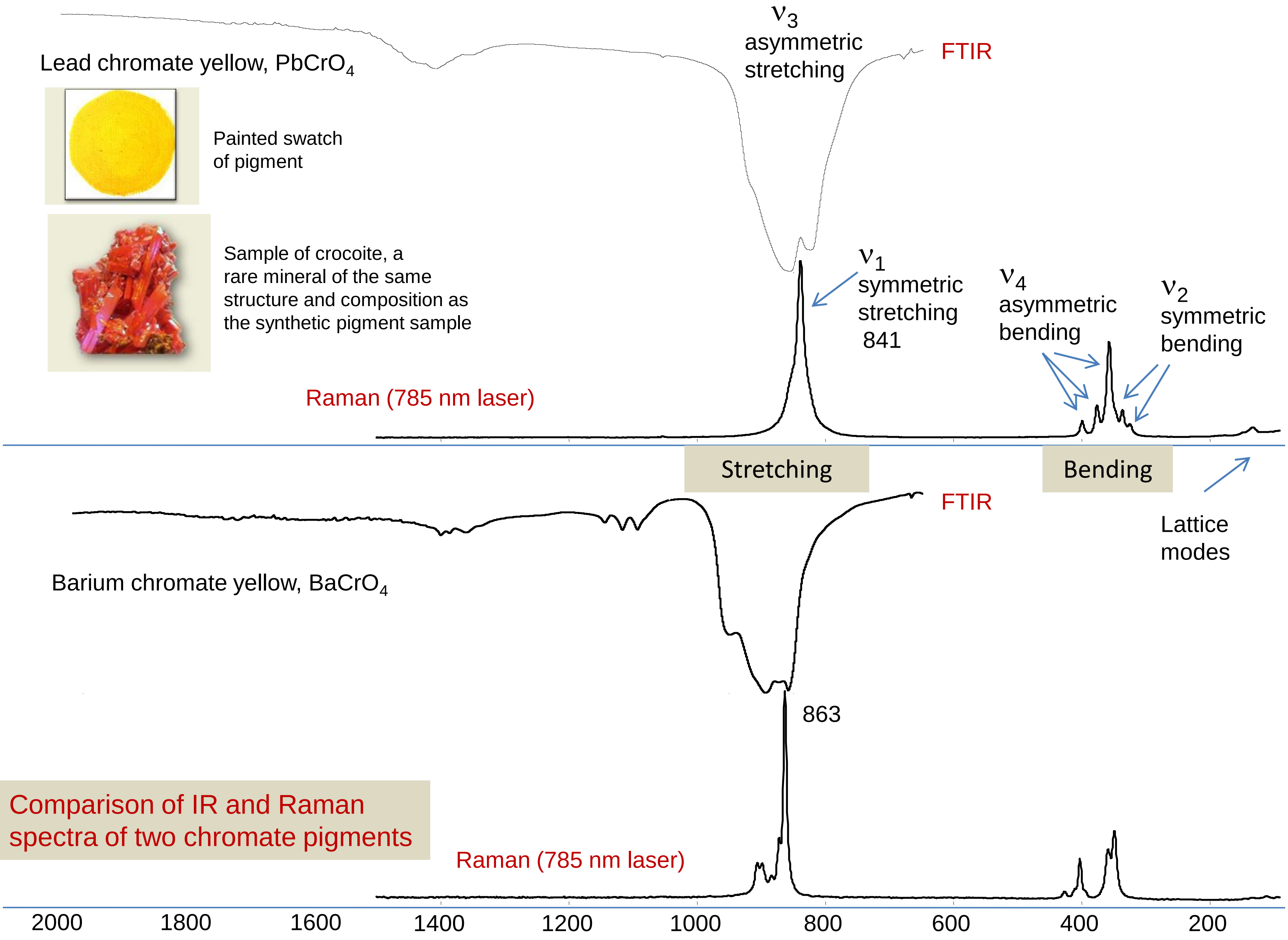
Comparison of IR and Raman spectra of BaSO$_4$

Comparison of IR and Raman spectra of gypsum $CaSO_4 \cdot 2H_2O$





FTIR spectrum
(4000-650 wavenumbers)



Comparison of IR and Raman spectra of two chromate pigments

Summary of spectral features of compounds containing polyatomic ions

Anhydrous compounds in IR

Often several absorption bands

Major one (asymmetric stretch) is quite broad, may have several distinctive shoulders

Anhydrous compounds in Raman

Usually one sharp band (symmetric stretch), other smaller (still sharp) ones; external vibration bands accessible

Compounds that contain hydroxyl groups or water of hydration

Additional bands in both IR and Raman; more complex spectra

Note:

- Peaks for a specific vibration mode (such as v_3) do not necessarily occur at exactly the same wavelength in Raman and IR
- Intensities of peaks may vary with laser wavelength
- Intensities of peaks may vary with crystal orientation for compound being analyzed
- Line widths can be affected by particle size and disorder

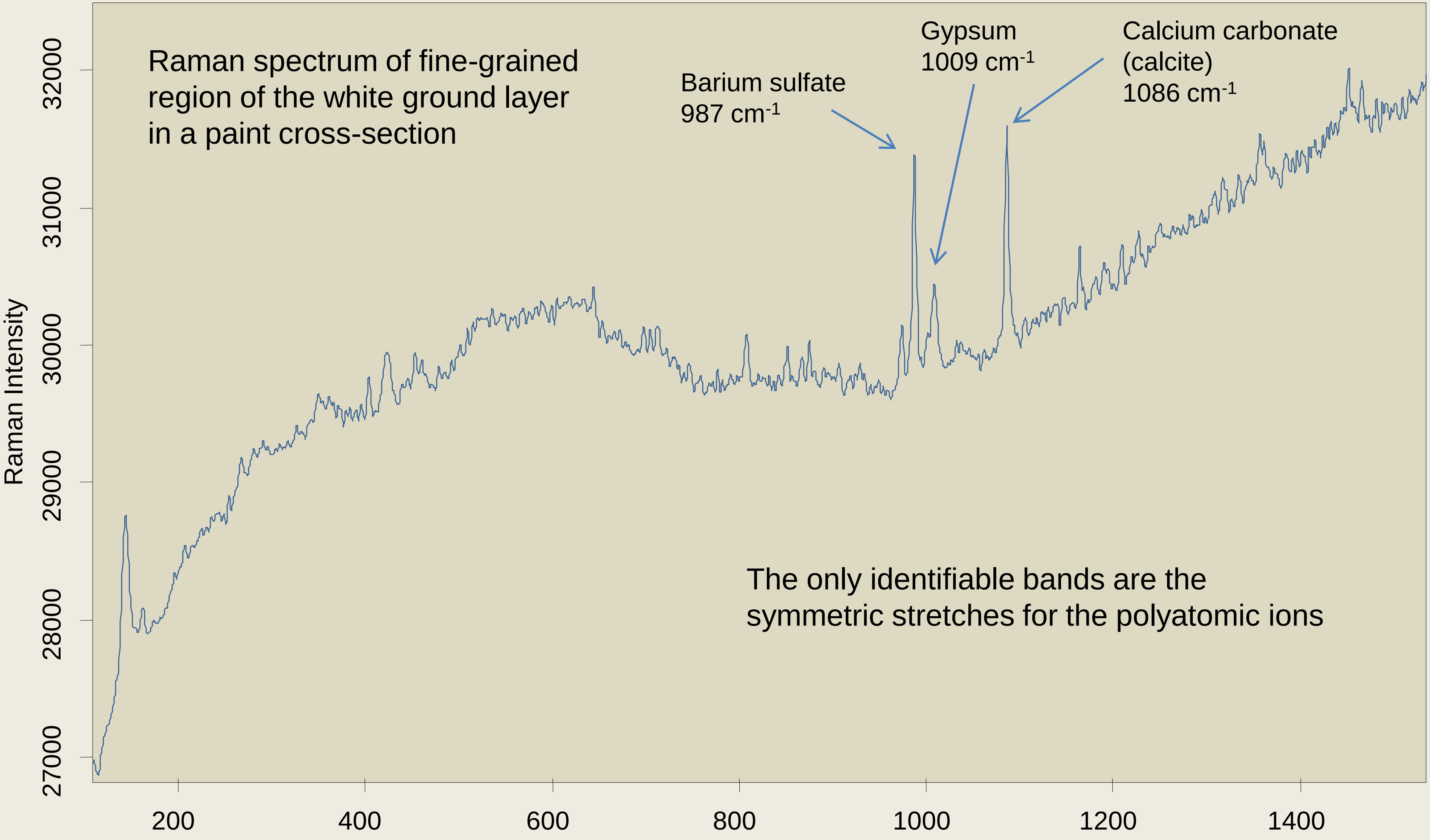
Certainty of identifications by Raman

Symmetric stretch is the largest, most readily noticed band in Raman spectra of compounds containing polyatomic ions – and it is sharp so its frequency can be very accurately noted

Not many compounds of a specific type have symmetric stretches at exactly the same position

Symmetric stretching vibration (Raman) in various sulfates

	cm^{-1}
Anhydrite, $CaSO_4$	1017
Bassanite, $CaSO_4$ hemihydrate	1015
Gypsum, $CaSO_4$ dihydrate	1008
Barite, $BaSO_4$	988
Anglesite, $PbSO_4$	981
Magnesium sulfates:	
Anhydrous	1023,1053
Monohydrate	1046
4 H_2O	1000
7 H_2O (epsomite)	984
11 H_2O	984



Raman spectrum of fine-grained region of the white ground layer in a paint cross-section

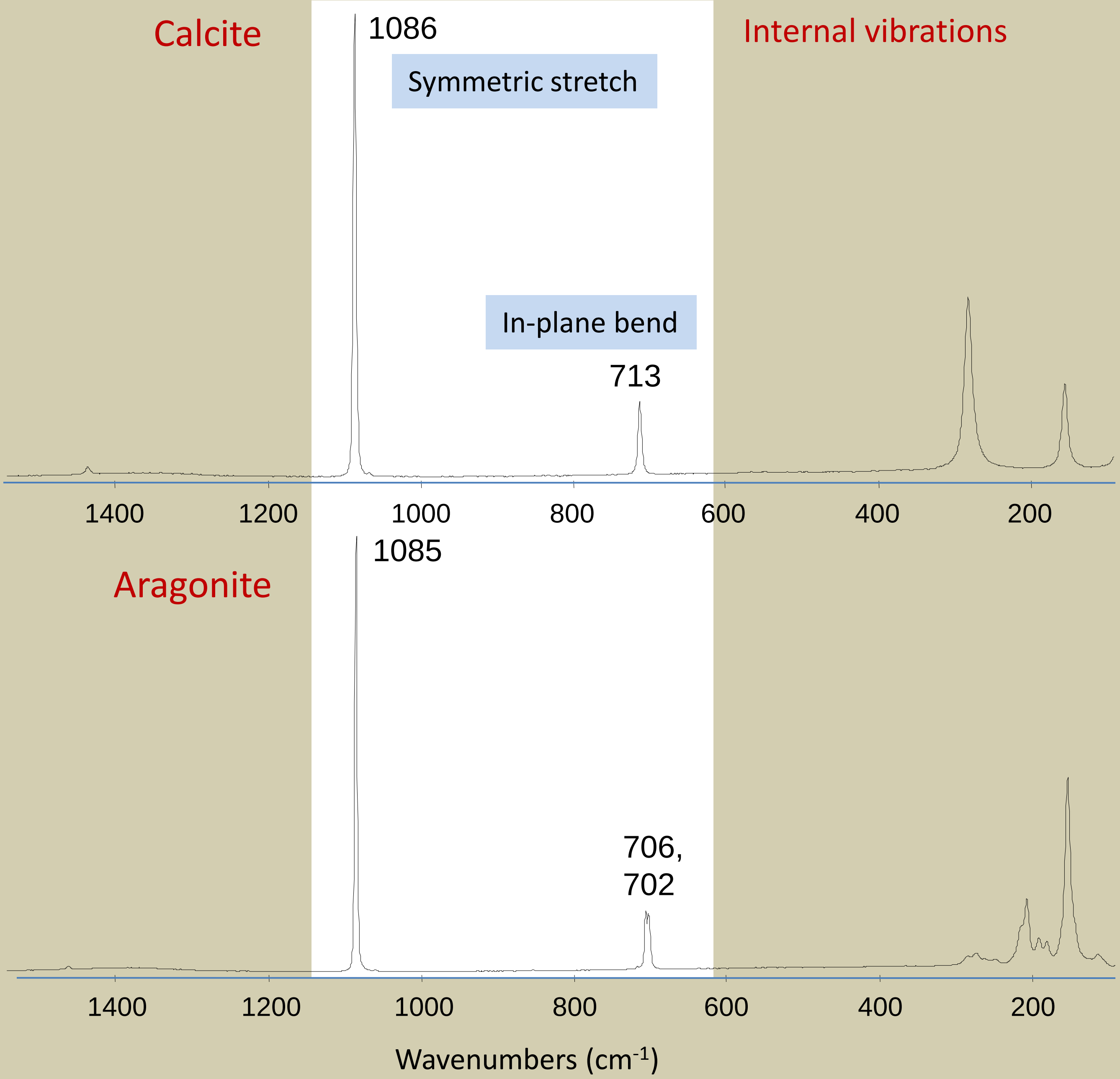
Barium sulfate 987 cm^{-1}

Gypsum 1009 cm^{-1}

Calcium carbonate (calcite) 1086 cm^{-1}

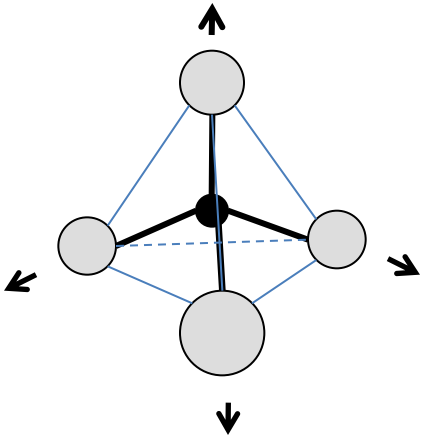
The only identifiable bands are the symmetric stretches for the polyatomic ions

785 nm laser, power on sample ~ 9.4 mW, acquisition time 60 seconds
50X objective, spot size ~ 2 microns
SEM/EDS analysis shows **S, Ca and Ba** as major elements; **Al, Si, Fe and Zn** as minor or trace elements


Calcite
1086
Symmetric stretch
Internal vibrations
In-plane bend
713
1400
1200
1000
800
600
400
200
1085
Aragonite
706,
702
1400
1200
1000
800
600
400
200
Wavenumbers (cm-1)

3. Silicates: a special type of polyatomic ion

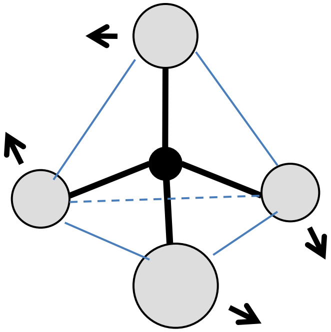
Isolated SiO_4 tetrahedron (4 modes, 9 total vibrations)



ν_1 (symmetric stretch)

Raman active (often strong)

800-950 cm-1

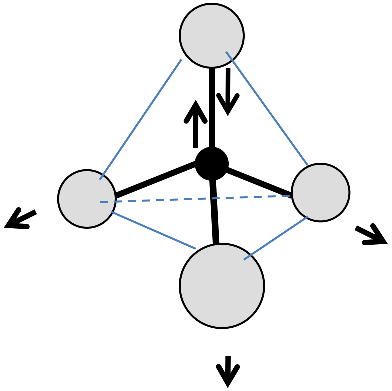


ν_2 (symmetric bend)

Doubly degenerate*;

Raman active

300-500 cm-1

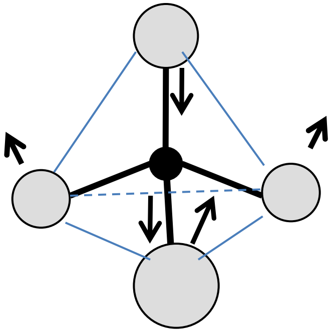


ν_3 (asymmetric stretch)

Triply degenerate*;

IR (strong) and Raman active

850-1200 cm-1



ν_4 (asymmetric bend)

Triply degenerate*;

IR and Raman active

400-600 cm-1

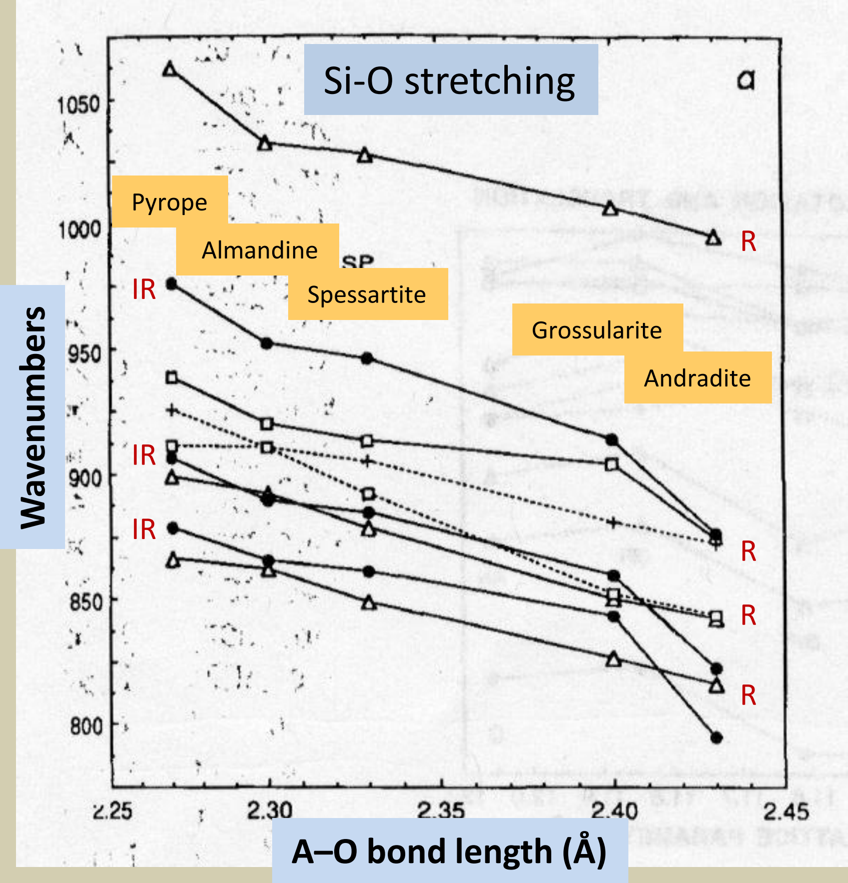
* Only one of the degenerate vibrations is shown

Almandine garnets

Pyrope (rhodolite variety) garnets

Garnets, $A_3B_2(SiO_4)_3$

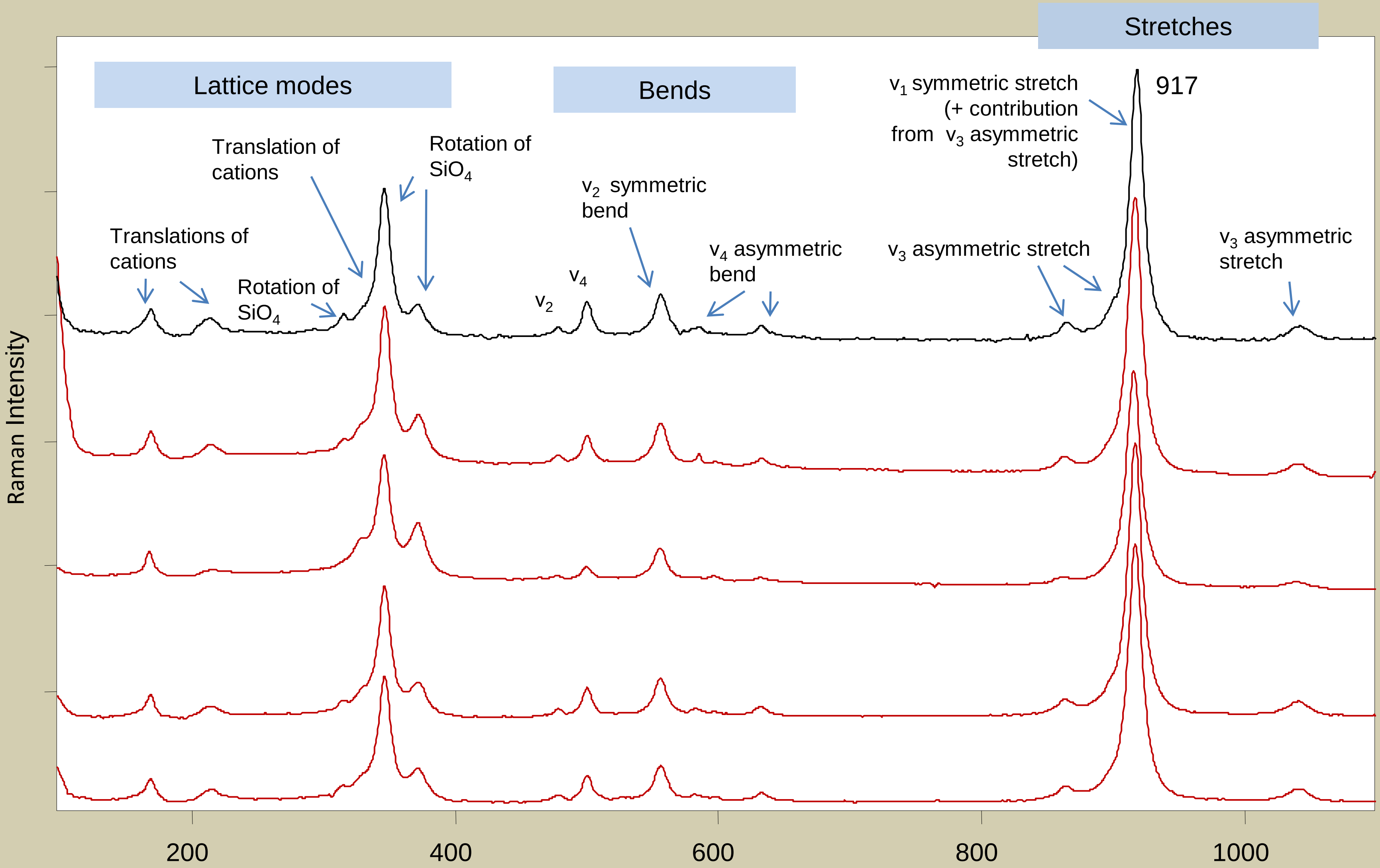
A site (larger 2+ cations) octahedral	B site (smaller 3+ cations) dodecahedral	Name
Pyralspite series (no Ca in A site; Al in B site)		
Fe	Al	almandine
Mg	Al	pyrope
Mn	Al	spessartite
Ugrandite (Ca in A site)		
Ca	Cr	uvarovite
Ca	Al	grossularite
Ca	Fe	andradite



ν_1(symmetric stretch) = dashed lines

ν_3(asymmetric stretch) = solid lines
Solid circles = IR-active bands; others are Raman-active

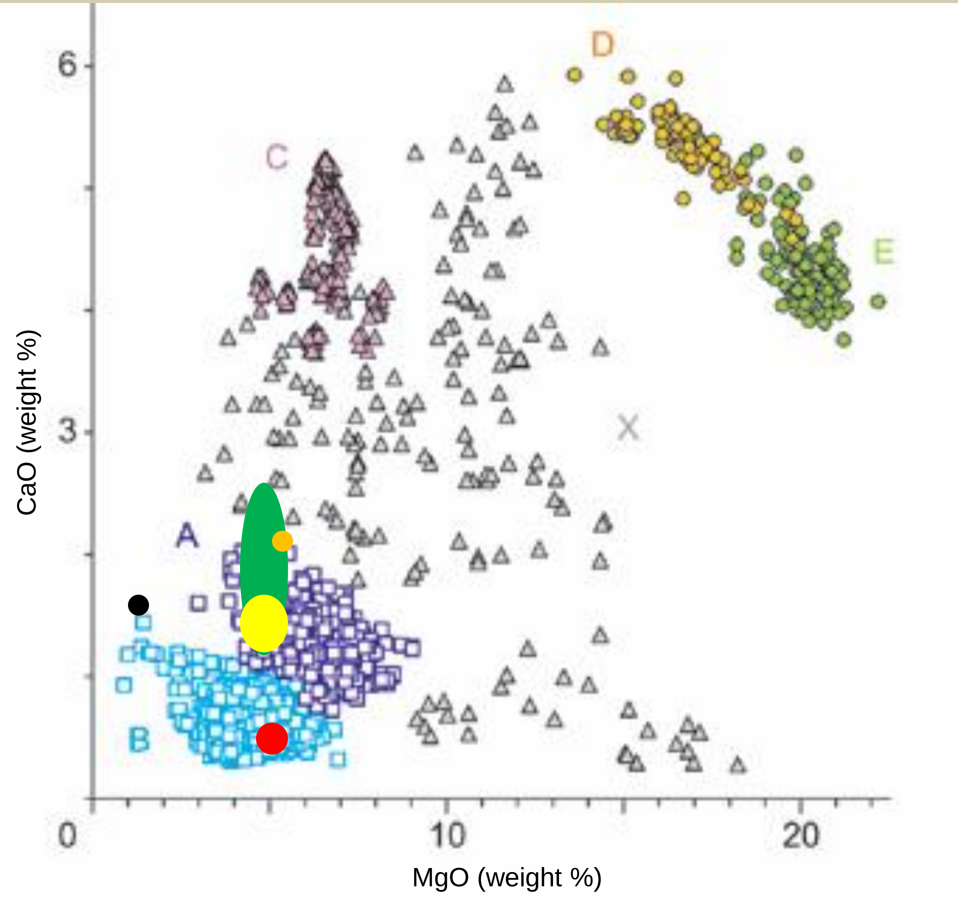
Graph from Hofmeister and Chopelas, *Physics and Chemistry of Minerals* 17 (1991): 503-526



Raman spectra (785 nm laser) of almandine garnets: top, sample from Rajmahal, India (courtesy of H. A. Gilg); bottom four, garnets from Deir El-Bersha, Middle Kingdom, Egypt, 1991-1783 BC

Band assignments from Hofmeister and Chopelas, *Physics and Chemistry of Minerals* 17 (1991): 503-526

Chart showing compositions of garnets in early Europe, ca. 500-650



Grossular and andradite →

Almandine: no Ca or Mg

Pyrope →

Five currently recognized compositional groups (A-E), based primarily on CaO, MgO and Cr_2O_3 contents

- ● Egyptian garnet beads, Middle Kingdom, 1991-1783 BC
- ● Egyptian garnet beads, Old Kingdom, 2323-2040 BC
- ● Egyptian garnet bead (1) Predynastic period, 3650-3300 BC,
- ● Garnet from Rajmahal, Jaipur state, India
- ● Almandine standard in Hofmeister and Chopelas

Chart from H.A. Gilg, N. Gast and Th. Calligaro, “Vom Karfunkelstein,” in *Karfunkelstein und Seide,* 2010, p. 95.

In most types of silicate minerals, the SiO_4 tetrahedra are 'polymerized' to various extents, from completely (all oxygens bonded to Si atoms, no non-bridging oxygens) to partially, with 1, 2 or 3 non-bridging oxygens (NBOs)

NBO = 0

Tectosilicates
(quartz, chalcedony,
feldspars)

NBO = 1

Phyllosilicates or
layer silicates
(micas, clays)

NBO = 1 to 2

Inosilicates, single chain
(pyroxenes, such as
jadeite)

NBO = 2

Cyclosilicates
(tourmaline; beryl)

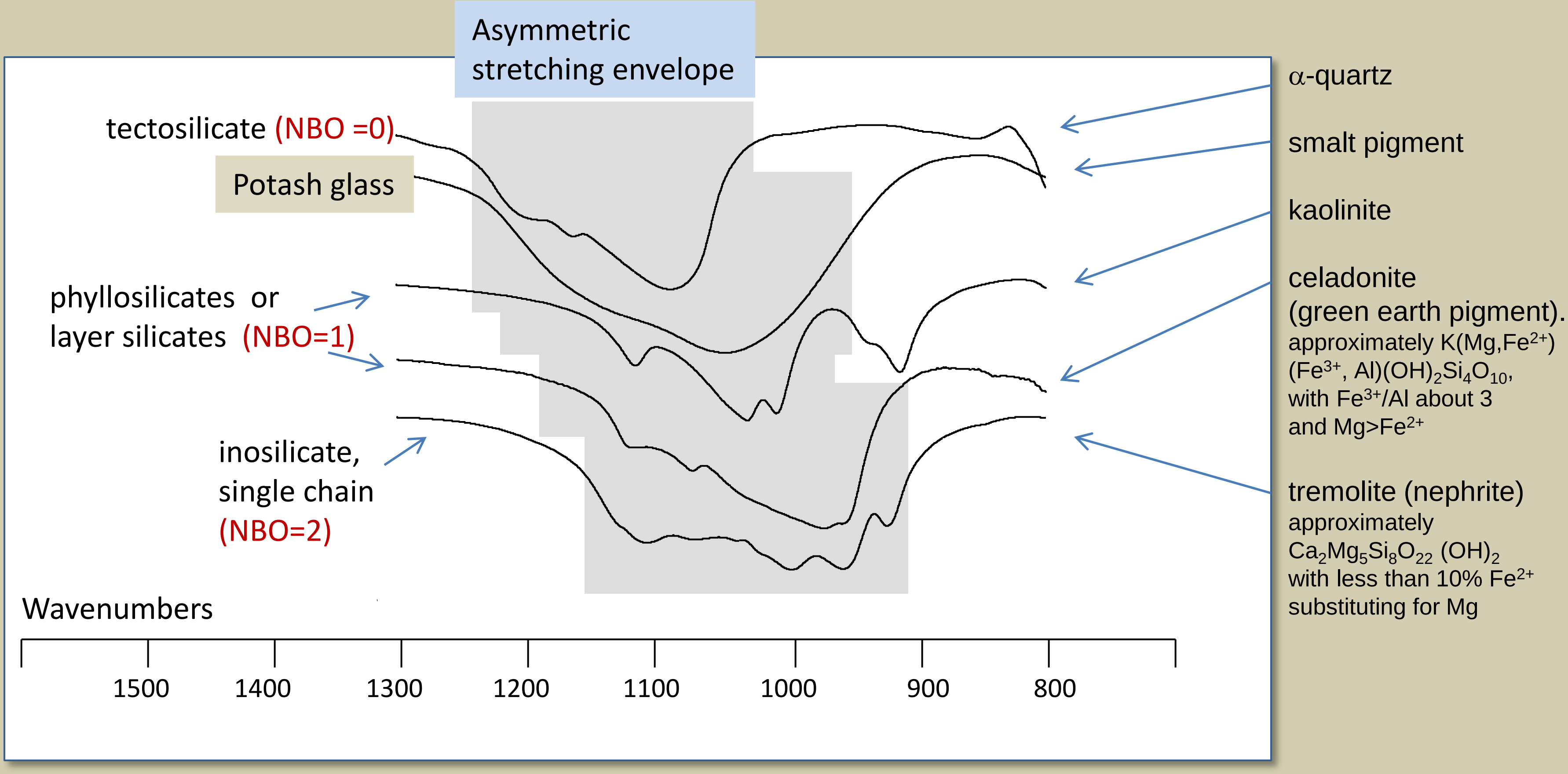
NBO = 2

Inosilicates, double chain
(amphiboles, such as
nephrite jade)

NBO = 3 Sorosilicates (epidote)

NBO = 4 Nesosilicates (garnets)

Asymmetric stretching vibrations (IR) of various silicates, including glass



tectosilicate (NBO =0)

Potash glass

phyllosilicates or layer silicates (NBO=1)

inosilicate, single chain (NBO=2)

α-quartz

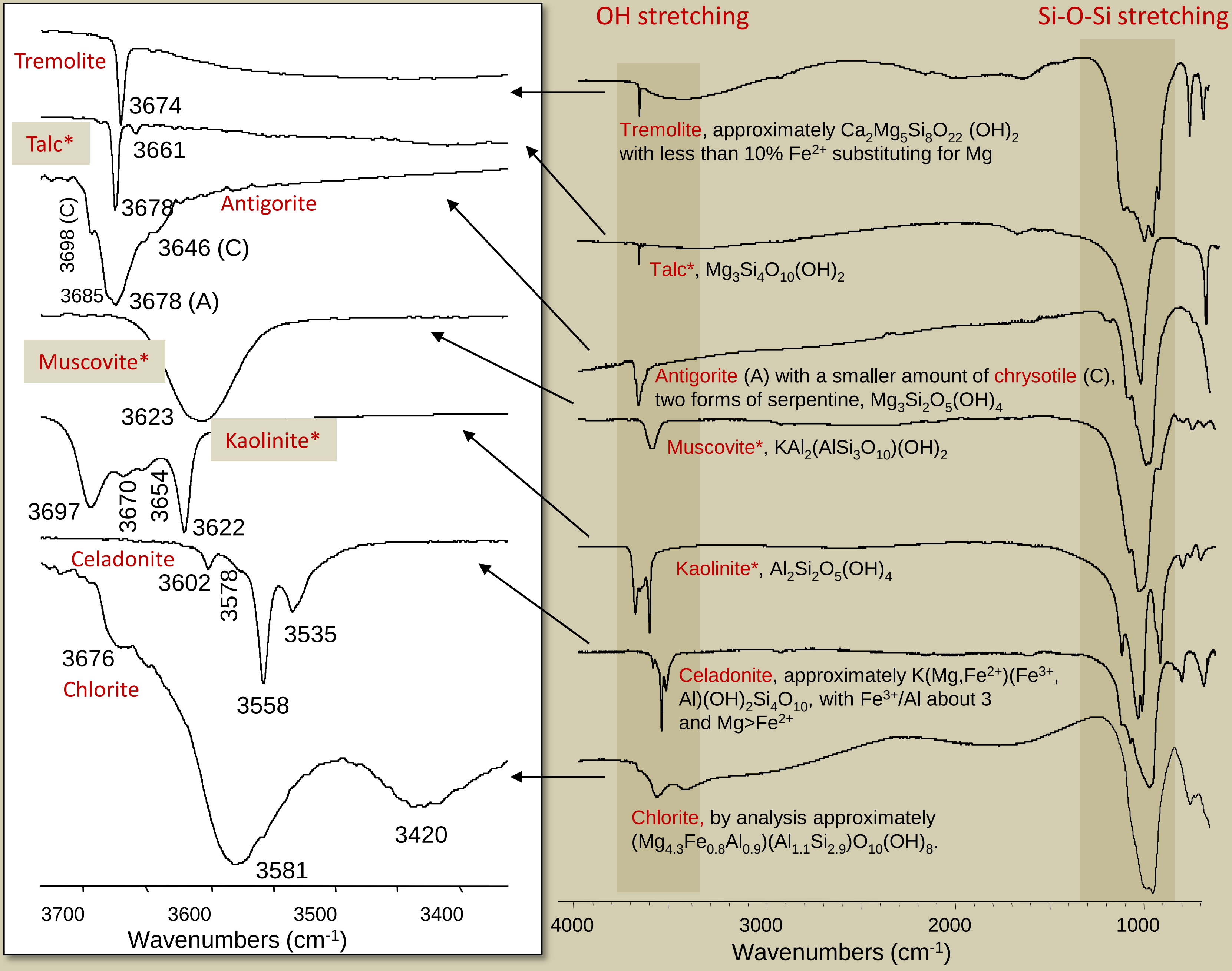
smalt pigment

kaolinite

celadonite (green earth pigment).
approximately K(Mg,Fe^{2+})(Fe^{3+}, Al)$(OH)_2Si_4O_{10}$,
with Fe^{3+}/Al about 3
and Mg>Fe^{2+}

tremolite (nephrite)
approximately
$Ca_2Mg_5Si_8O_{22}$ $(OH)_2$
with less than 10% Fe^{2+}
substituting for Mg

General class of silicate often can be identified from the asymmetric stretching region, and sometimes a specific identification can be made



Tremolite, approximately $Ca_2Mg_5Si_8O_{22}(OH)_2$ with less than 10% Fe^{2+} substituting for Mg

Talc*, $Mg_3Si_4O_{10}(OH)_2$

Antigorite (A) with a smaller amount of chrysotile (C), two forms of serpentine, $Mg_3Si_2O_5(OH)_4$

Muscovite*, $KAl_2(AlSi_3O_{10})(OH)_2$

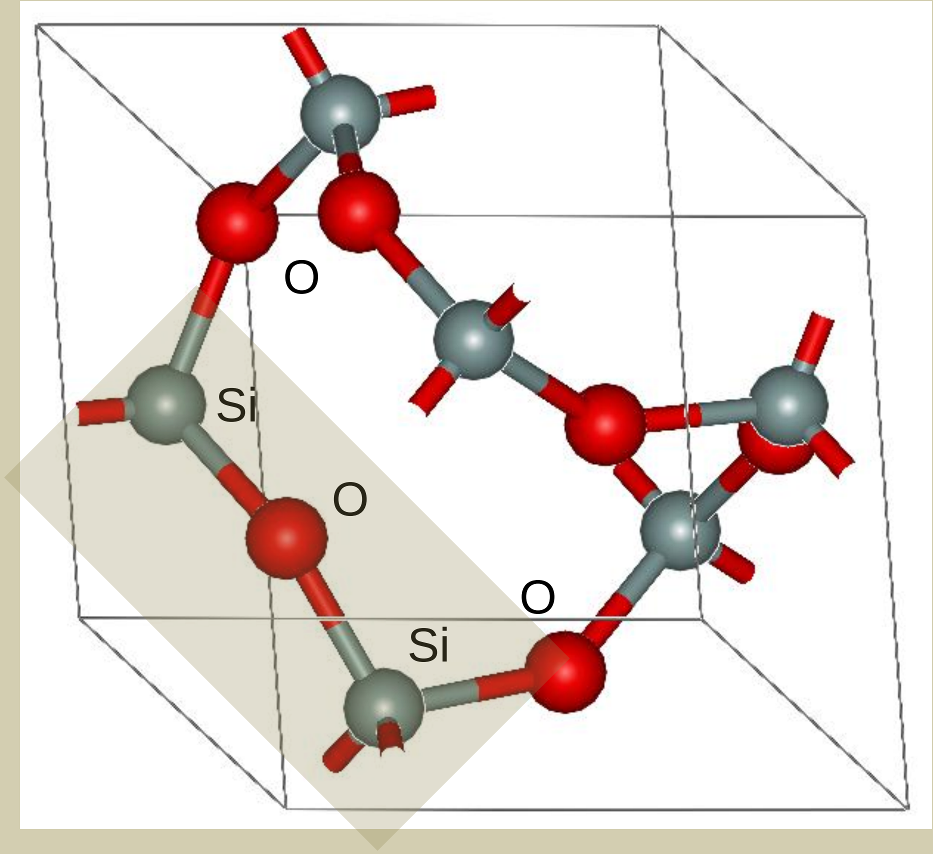
Kaolinite*, $Al_2Si_2O_5(OH)_4$

Celadonite, approximately $K(Mg,Fe^{2+})(Fe^{3+},Al)(OH)_2Si_4O_{10}$, with Fe^{3+}/Al about 3 and $Mg>Fe^{2+}$

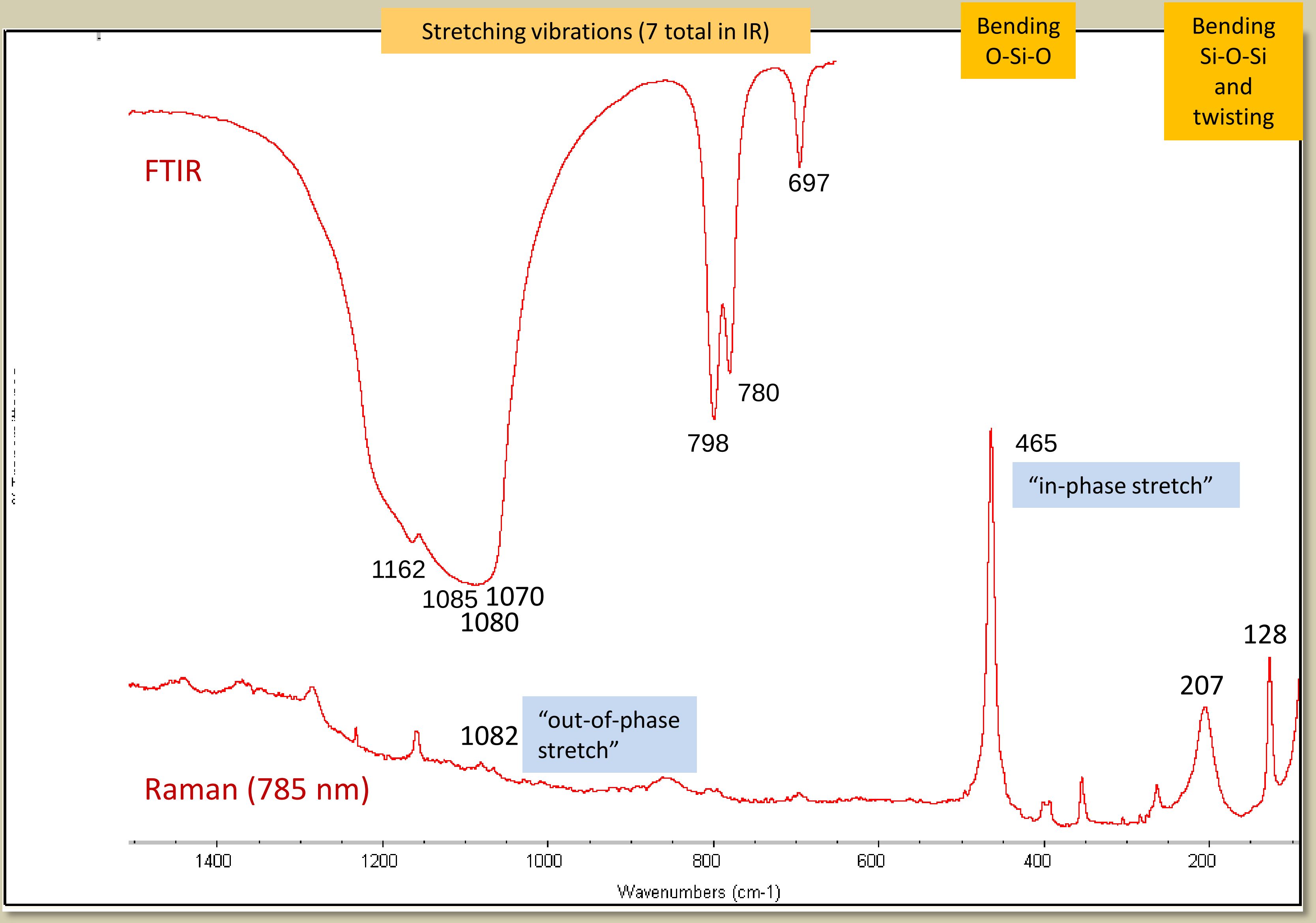
Chlorite, by analysis approximately $(Mg_{4.3}Fe_{0.8}Al_{0.9})(Al_{1.1}Si_{2.9})O_{10}(OH)_8$.

* Minerals with essentially fixed compositions

Structure of α-quartz (6-membered rings of SiO_4 tetrahedra), O-Si-O bond angle is 144°
NBO=0



Source of diagram: Wikipedia

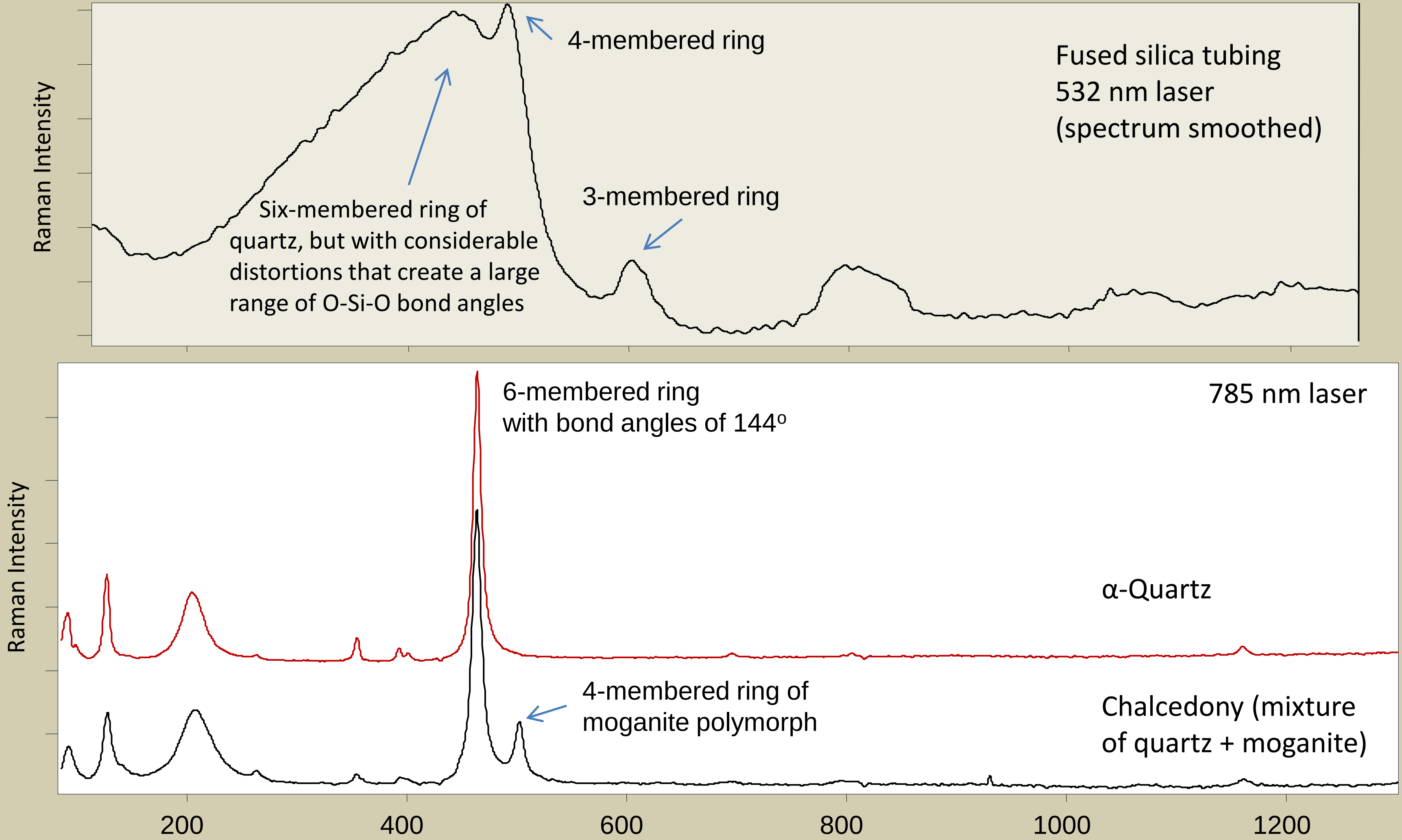


IR and Raman spectra of α-quartz

🟧 Vibrational mode designations from Etchepare et al., *Journal of Chemical Physics* 60 (1974): 1873-1876

🟦 Designations from McMillan , *American Mineralogist* 69 (1984): 622-644

Raman spectra of fused silica (glass), quartz and chalcedony



4-membered ring

Fused silica tubing
532 nm laser
(spectrum smoothed)

3-membered ring

Six-membered ring of quartz, but with considerable distortions that create a large range of O-Si-O bond angles

6-membered ring
with bond angles of 144°

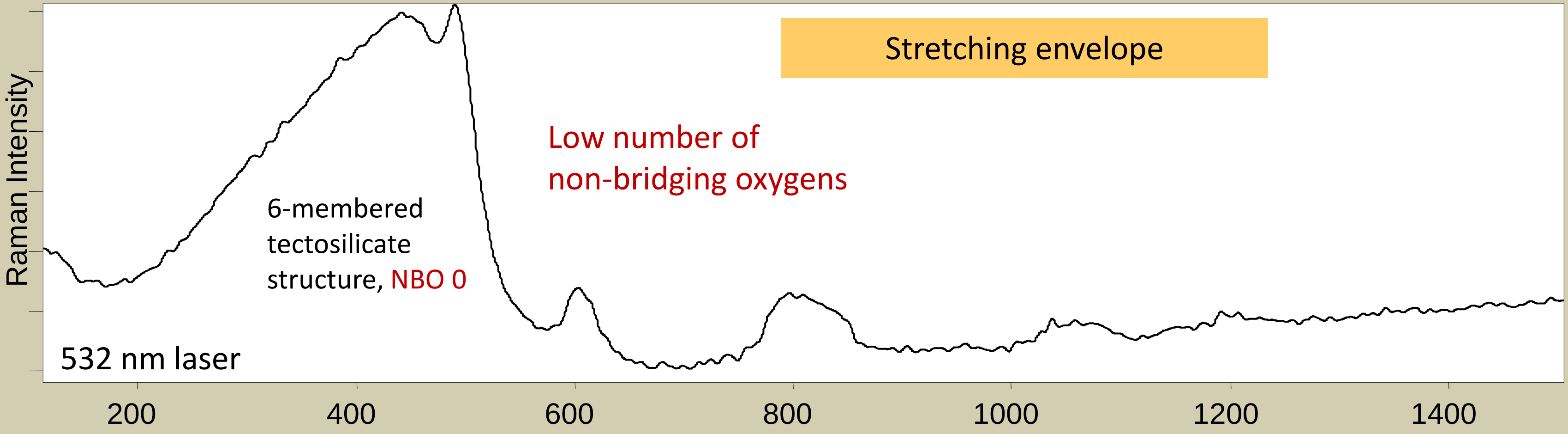
785 nm laser

α-Quartz

4-membered ring of
moganite polymorph

Chalcedony (mixture
of quartz + moganite)

Raman spectra of fused silica and Corning glass standard A

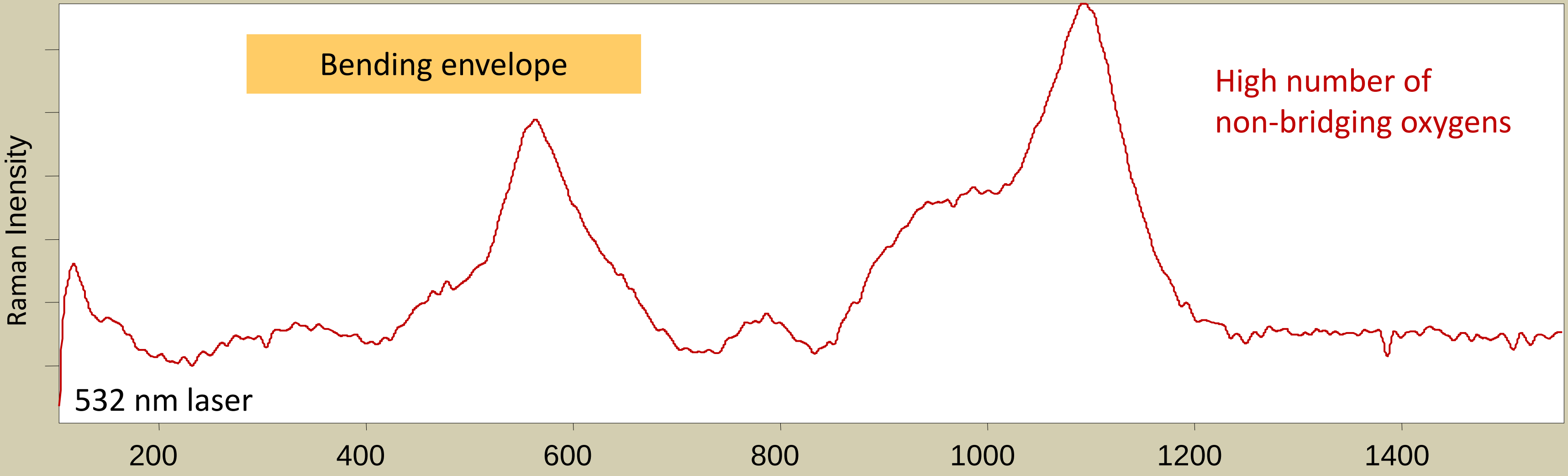


Stretching envelope

Low number of
non-bridging oxygens

6-membered
tectosilicate
structure, NBO 0

532 nm laser



Bending envelope

High number of
non-bridging oxygens

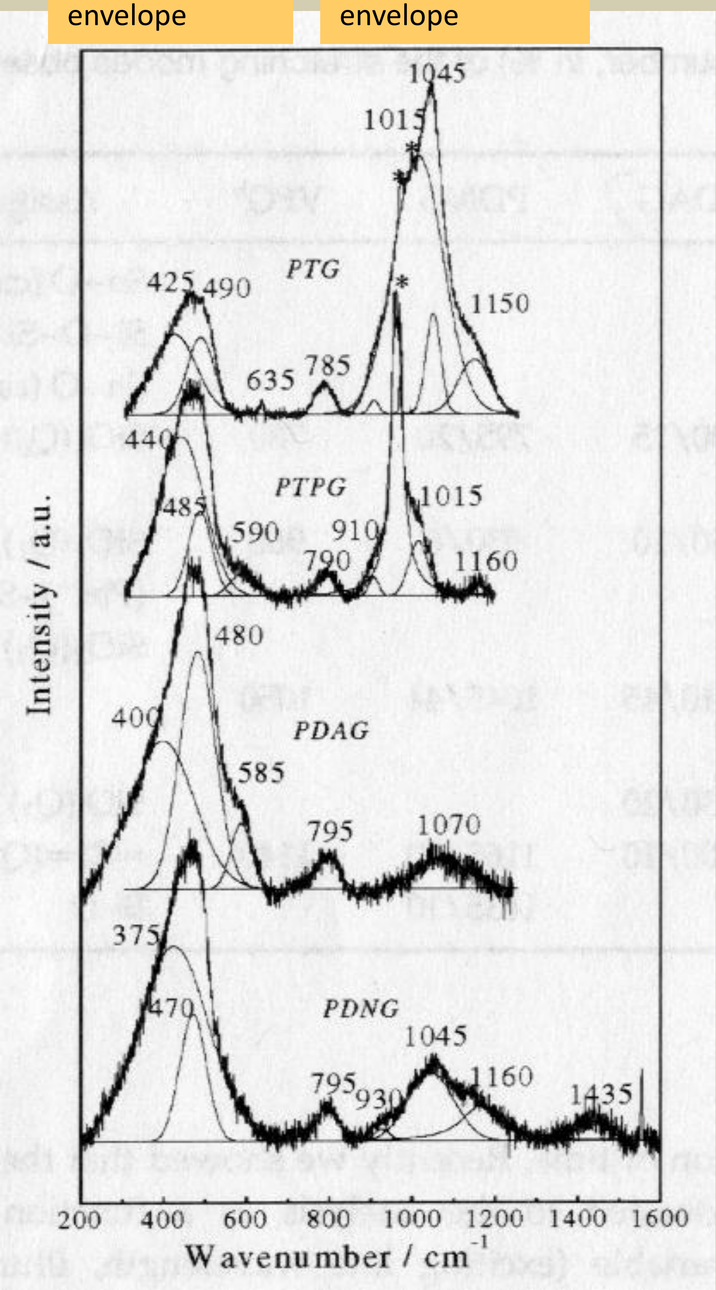
532 nm laser

Porcelain glazes

Some also contain crystalline phases (bands indicated by *)

Si-O-Si bending envelope

Si-O-Si stretching envelope



French soft-paste glaze(Pb/Si), fired at 1000°C

3-D framework more broken down

English-like soft-paste glaze(Pb/Si), fired at 1120°C

Hard porcelain glaze, fired at 1400°C

More "tectosilicate -like" (e.g. quartz)

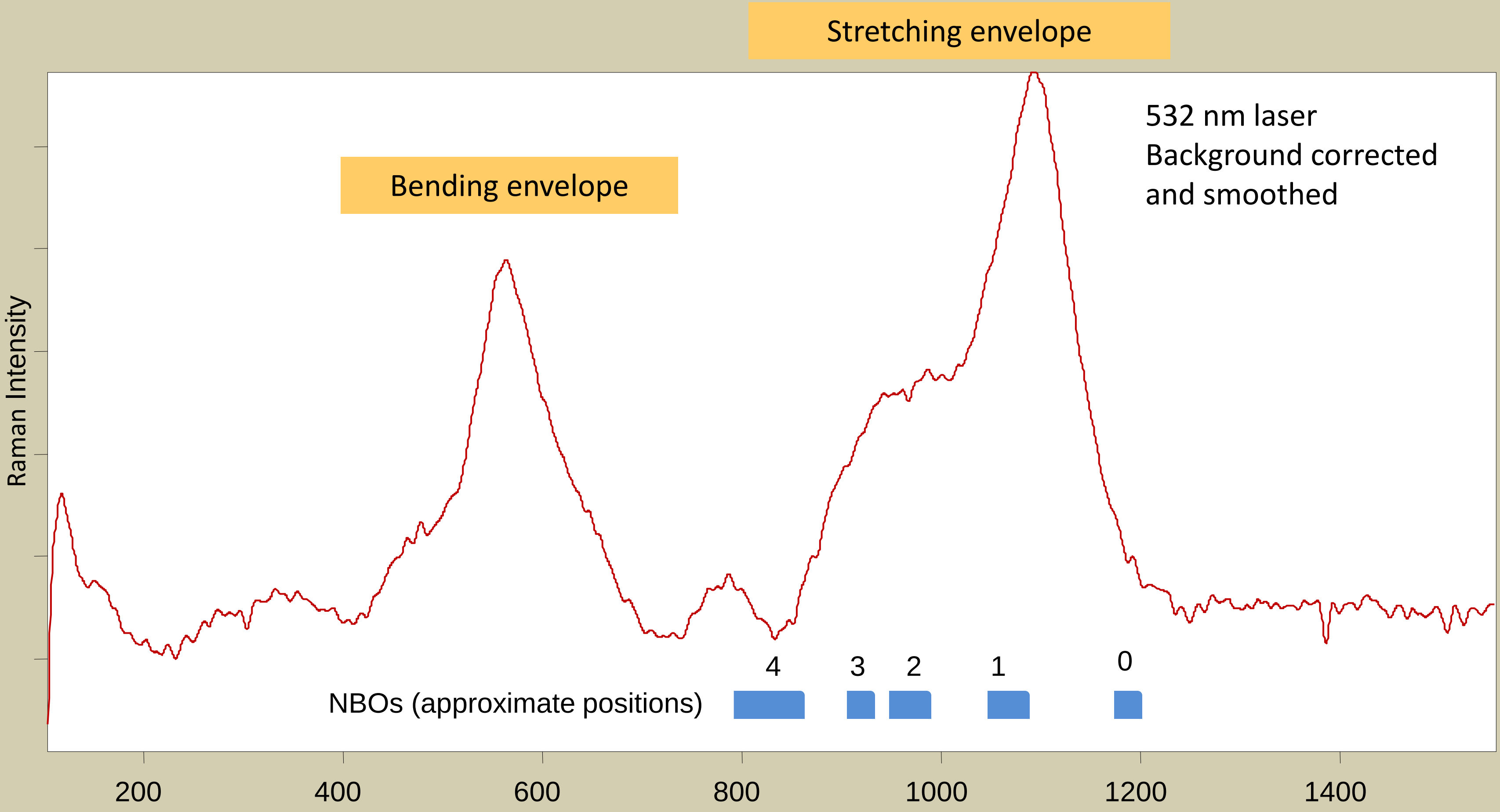
Hard porcelain glaze, fired at 1280°C

Spectra from Colomban and Treppoz, *Journal of Raman Spectroscopy* 32 (2001): 93-102

Corning glass A

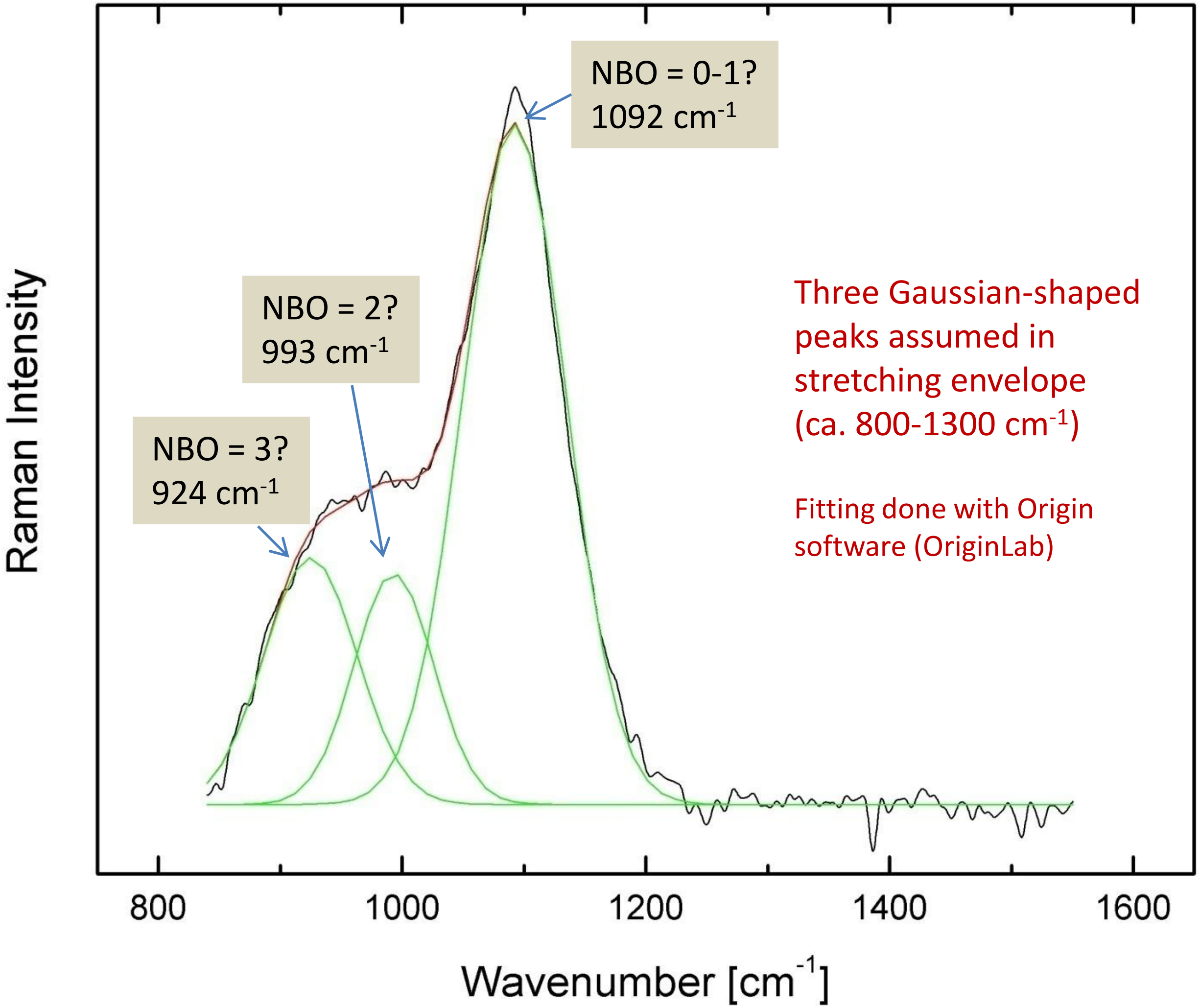
Composition: Na_2O 14.5%, SiO_2 66.6%, Al_2O_3 1.0%, MgO 2.8%, K_2O 2.9%, CaO 5.3%

Positions of bands for different NBOs from Mysen et al., *American Mineralogist* 65 (1980): 697



532 nm laser
Background corrected
and smoothed

Curve fitting to show contributions of different NBO structures to glass



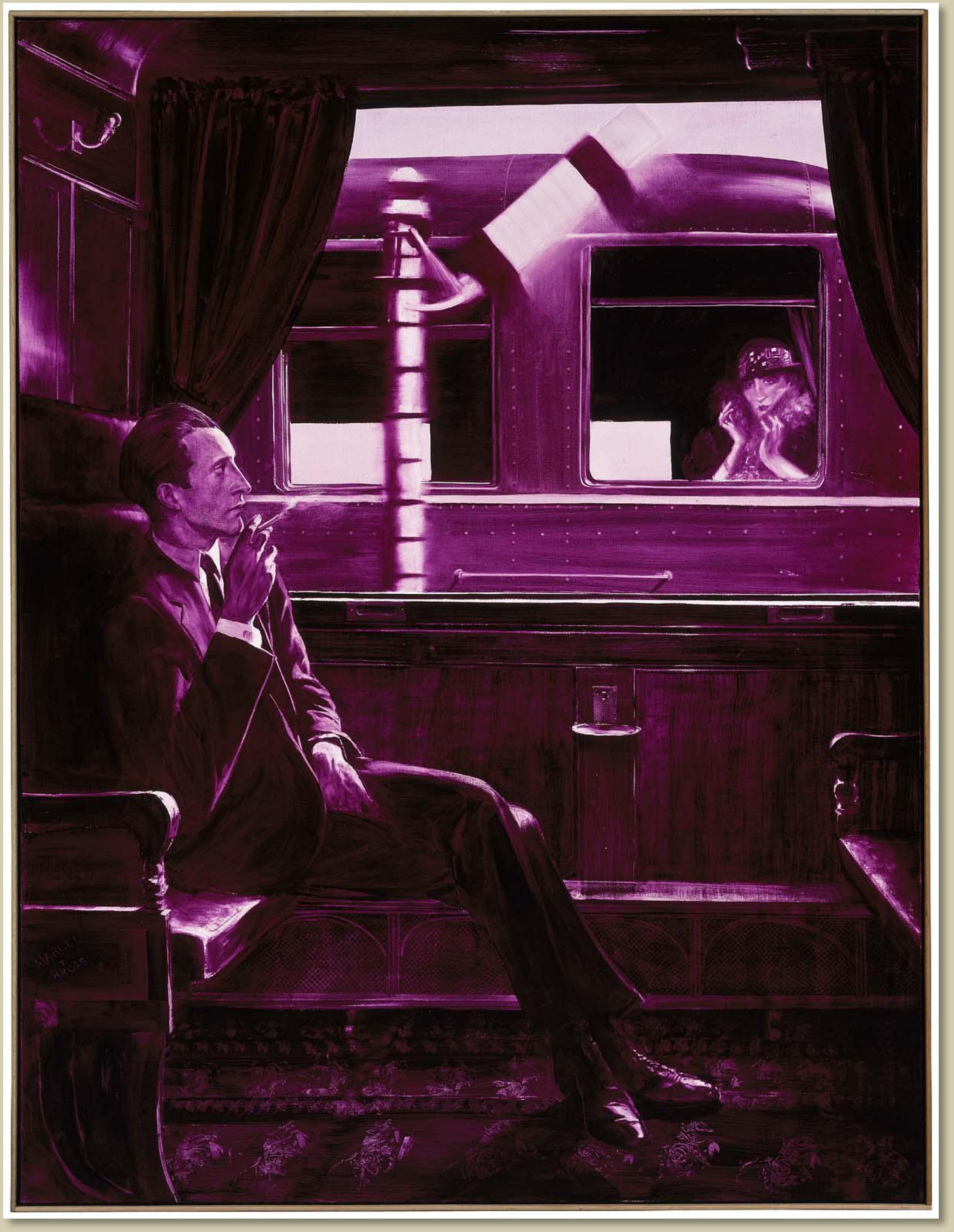
NBO = 0-1?
1092 cm^{-1}

NBO = 2?
993 cm^{-1}

NBO = 3?
924 cm^{-1}

Three Gaussian-shaped peaks assumed in stretching envelope (ca. 800-1300 cm^{-1})

Fitting done with Origin software (OriginLab)

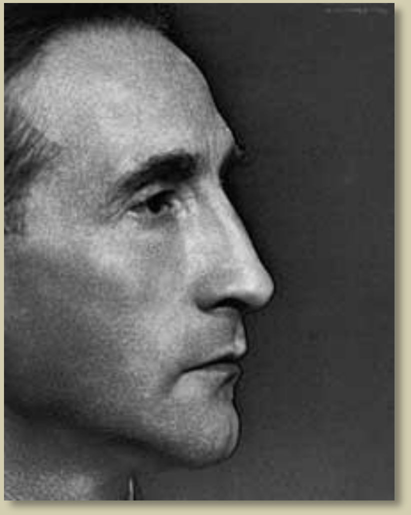


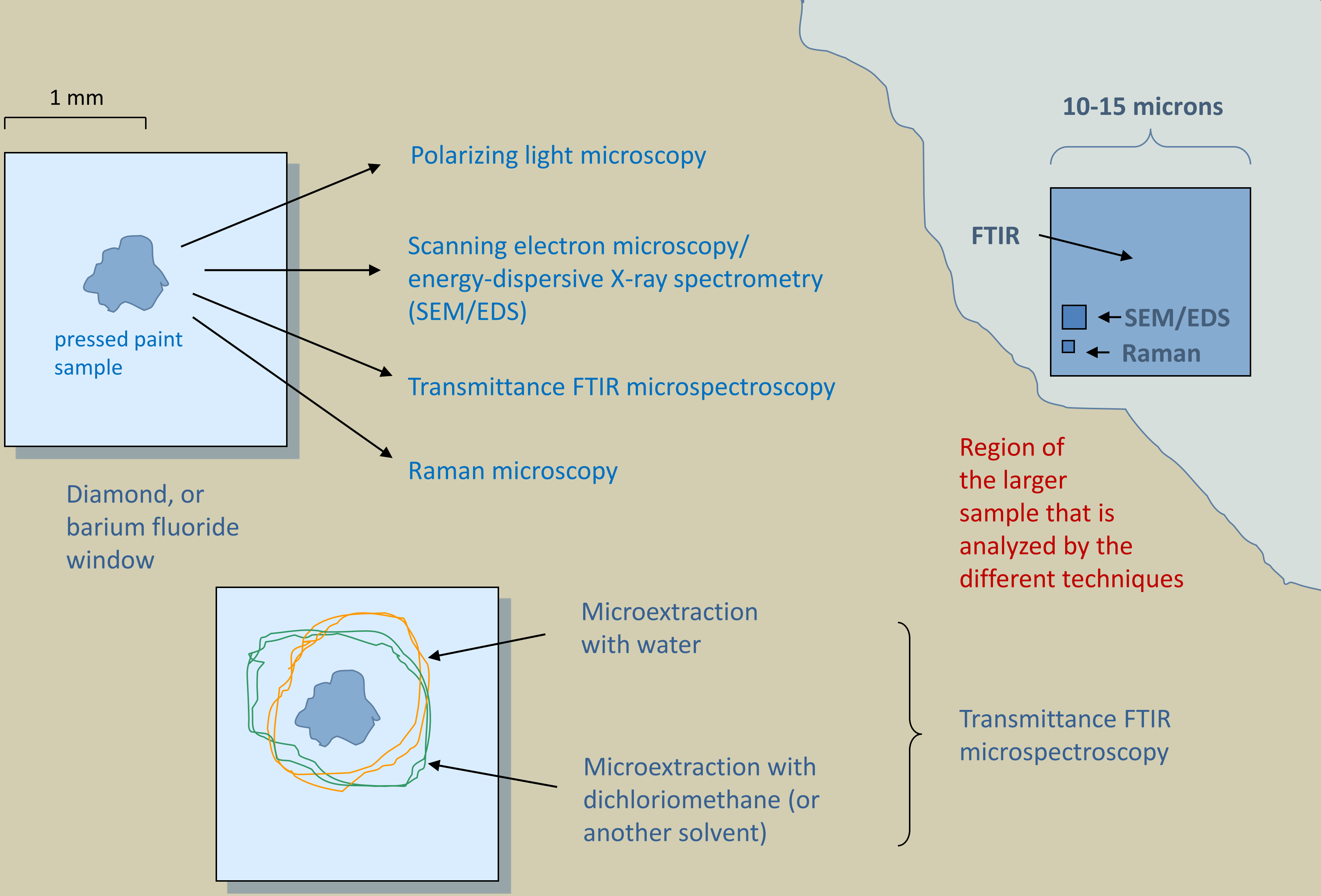
Mark Tansey, American
The Enunciation, 1992

Museum of Fine Arts, Boston
accession no. 1992.251

Photographs by Man Ray of Rrose Sélavy ("eros, c'ést la vie"), aka Marcel Duchamp

and Marcel Duchamp





1 mm

pressed paint sample

Diamond, or barium fluoride window

Polarizing light microscopy

Scanning electron microscopy/ energy-dispersive X-ray spectrometry (SEM/EDS)

Transmittance FTIR microspectroscopy

Raman microscopy

10-15 microns

FTIR

SEM/EDS

Raman

Region of the larger sample that is analyzed by the different techniques

Microextraction with water

Microextraction with dichloriomethane (or another solvent)

Transmittance FTIR microspectroscopy

White pigments and fillers (4)

Zinc oxide ●
Barium sulfate ▲ ●
Calcium carbonate (calcite) ▲ 🟩 ●
Calcium magnesium carbonate (dolomite) ▲

Colored pigments (7)

Ultramarine blue (synthetic) ▲
Two types of cobalt violet (with different Co/P ratios) 🟩 ●
Organic red (hydroxyanthraquinone, possibly alizarin) on alumina substrate ▲●
Phthalocyanine blue ▲
Dioxazine violet ▲
Unidentified manganese-containing pigment (manganese violet?) ●

Binding medium: oil 🟩

Combined analytical techniques: polarized light microscopy (PLM), FTIR microspectroscopy 🟩, Raman microscopy ▲, scanning electron microscopy /energy-dispersive X-ray spectrometry (SEM/EDS) ●

All analyses carried out on one sample pressed on a diamond window

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman analysis of museum objects: advantages, limitations & practical tips

Lucia Burgio

Victoria and Albert Museum, London, UK

THURSDAY, SEPTEMBER 27: LECTURE 5

Raman analysis of museum objects: advantages, limitations and practical tips

Lucia Burgio
Conservation Department, Science Section

IRUG Raman Spectroscopy Workshop
27-28 September 2012

Infrared and Raman Users Group
A collaboration to encourage the exchange of information, develop IR and Raman spectral standards, and distribute comparative spectral data for the study of works of art, architecture, and archeological materials.

Contents

- Raman analysis of Museum objects
- Microscope configurations
- Experimental conditions selection
- Limitations
- Practical examples

Raman analysis of Museum objects

Wide variety of substrates and materials:










Full characterisation

Pigments in aqueous media:
Manuscripts
Miniatures
Watercolours

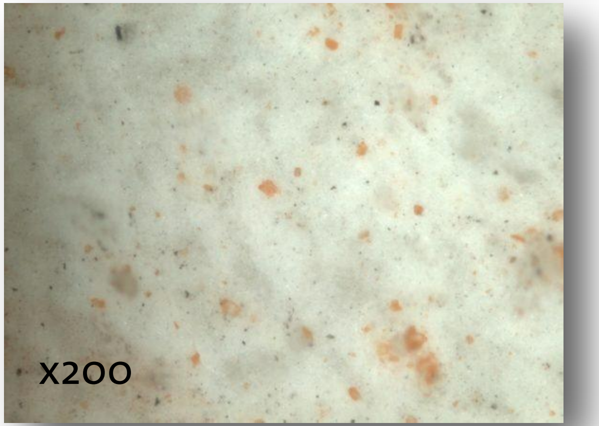
Paintings

IN SITU

SAMPLING NEEDED

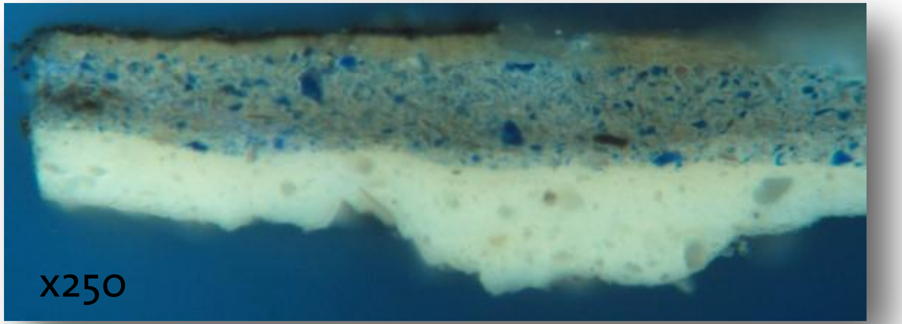
Full characterisation

Pigments in aqueous media:
Manuscripts
Miniatures
Watercolours



IN SITU

Paintings



SAMPLING NEEDED

Partial characterisation

Ceramics and glass

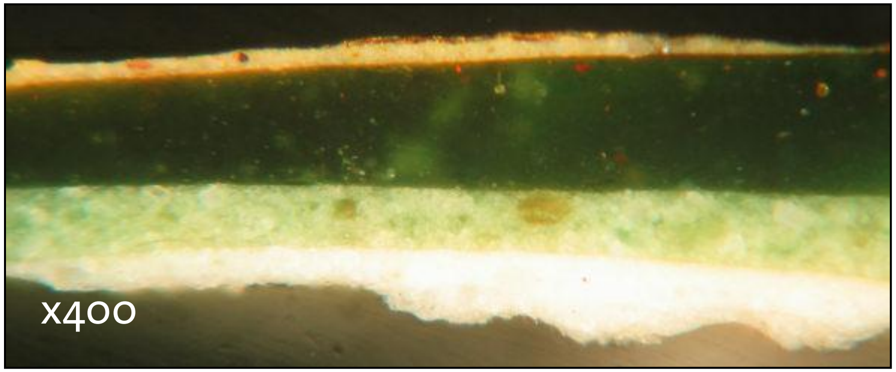
Furniture

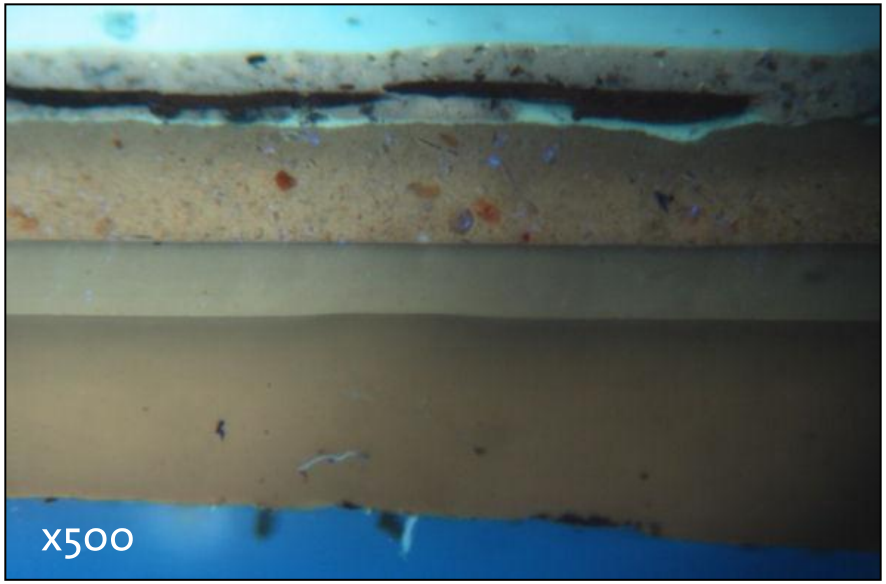
IN SITU

SAMPLING NEEDED

Partial characterisation

Furniture





Pigments/dyes
Varnishes

Lacquer
Varnishes
Metals

Partial characterisation

Textiles:
Dyes and pigments
(Fibres)

Metalwork

IN SITU or SAMPLING

IN SITU or SAMPLING

Why Raman microscopy?

Dating and Authentication

Attribution

Conservation

Provenancing and trade routes

Display conditions

Raman is....

Non-intrusive

Non-destructive

Specific

Fast

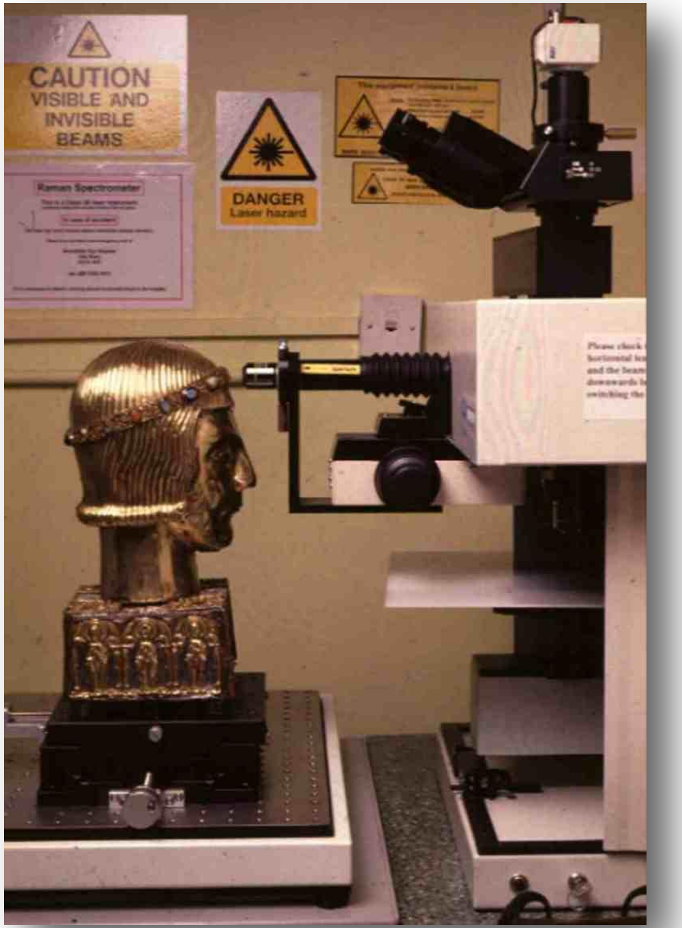
Microscopes' configurations

Traditional set up:
the V&A XploRA (Horiba)

Cradle for use with a Raman probe

Microscopes' configurations

Horizontal objectives



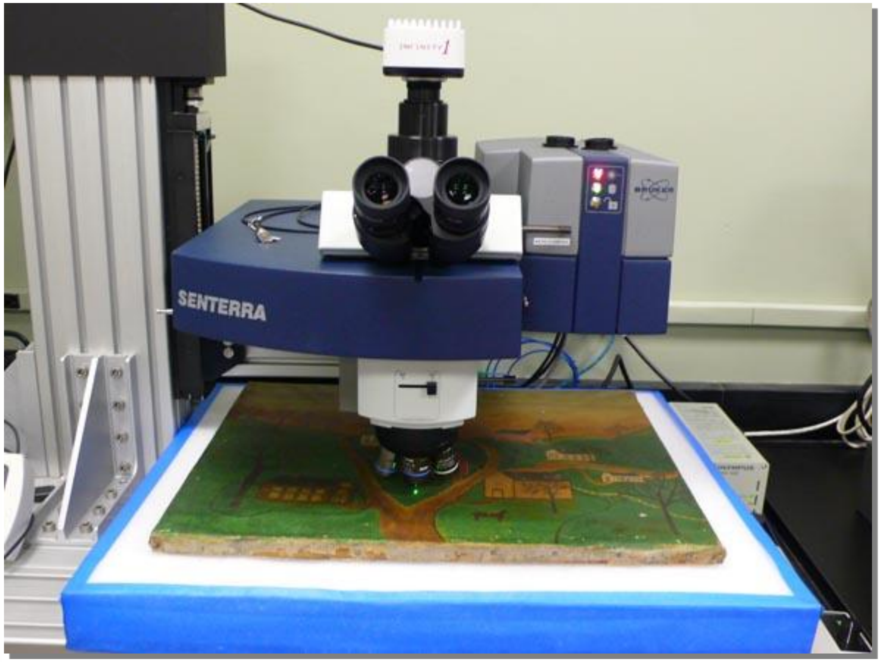
British Museum
(Dilor)

Getty
(Renishaw)

Microscopes' configurations

Open space architecture

Renishaw



Bruker Senterra
Buffalo State University, NY

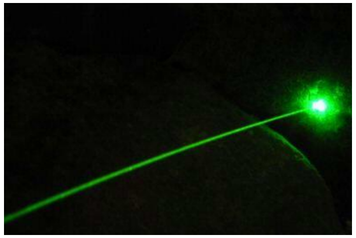
Choice of wavelength

Laser colour	Laser type	Acronym	Laser Wavelength
Blue	Argon ion	Ar ion	488.0 nm
Green	Argon ion	Ar ion	514.5 nm
	Solid state	-	532 nm
	Neodymium-doped yttrium aluminium garnet ($Nd:Y_3Al_5O_{12}$)	Nd:YAG	532 nm
Red	Helium-Neon	He-Ne	632.8 nm
	Solid state	-	~633 nm
	Krypton ion	Kr ion	647.1 nm
Far red	Solid state	-	780-785 nm
Near infrared	Neodymium-doped yttrium aluminium garnet ($Nd:Y_3Al_5O_{12}$)	Nd:YAG	1064 nm

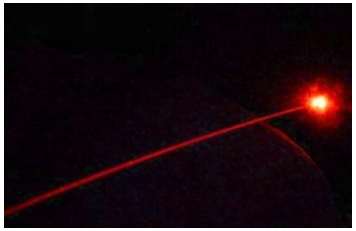
Choose wavelength as close in colour as possible to the colour of your sample!

Choice of wavelength

IR laser → Organic dyes and materials, polymers, fibres



→ Green, blue, white
(and yellow)



→ Pink, red, orange, yellow, white
(blue, green, black)

→ Most organic materials, dyes etc.

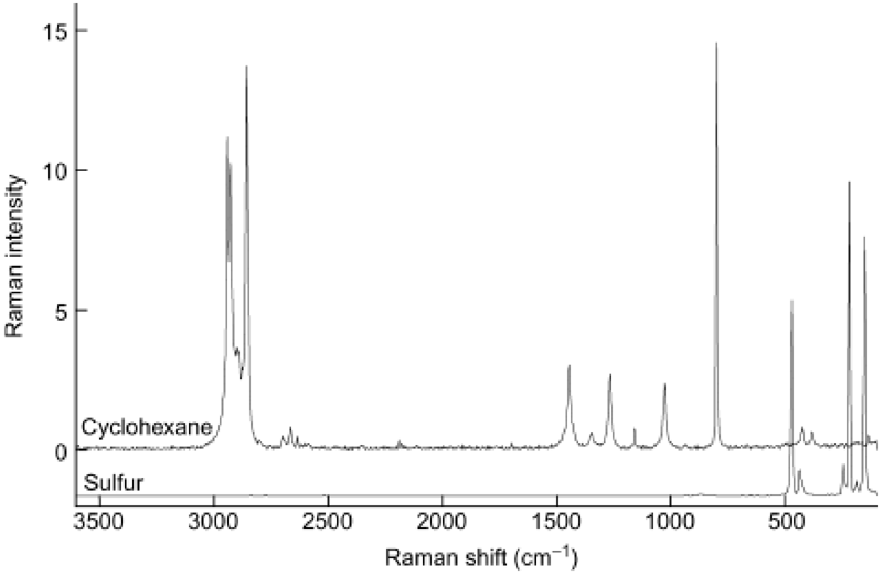
If you have money only for one laser, get a true red one!

Choice of experimental conditions

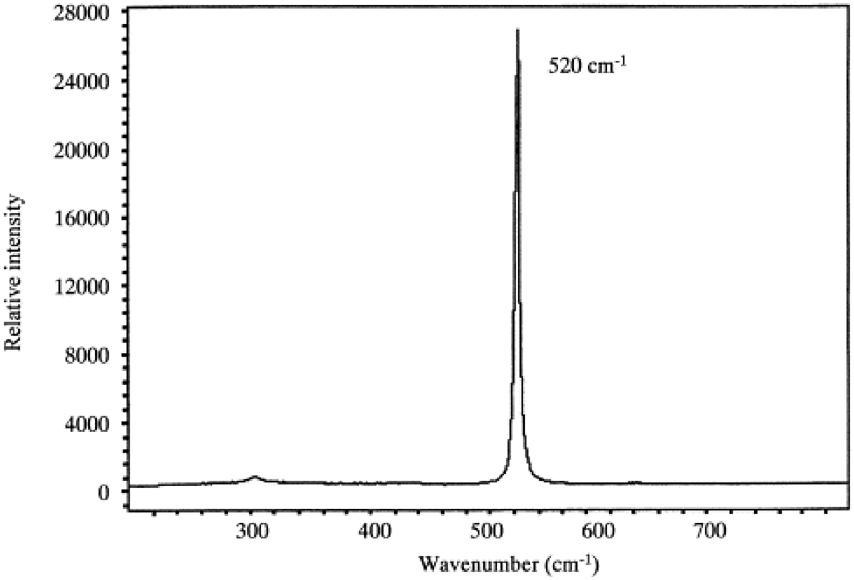
- Choose area and focus with x10 objective
- Pass to x50 or x100 objective and select crystal
- Use lowest possible power (1% is enough)
- Start with a short series of quick scans
- Stop and check your sample: did it burn?
- Select final condition, collect and save

Routine calibration

Start of the day: silicon or sulfur (cyclohexane)



http://mtnviewfarm.net/drugs-poisons-9025f006_1.html

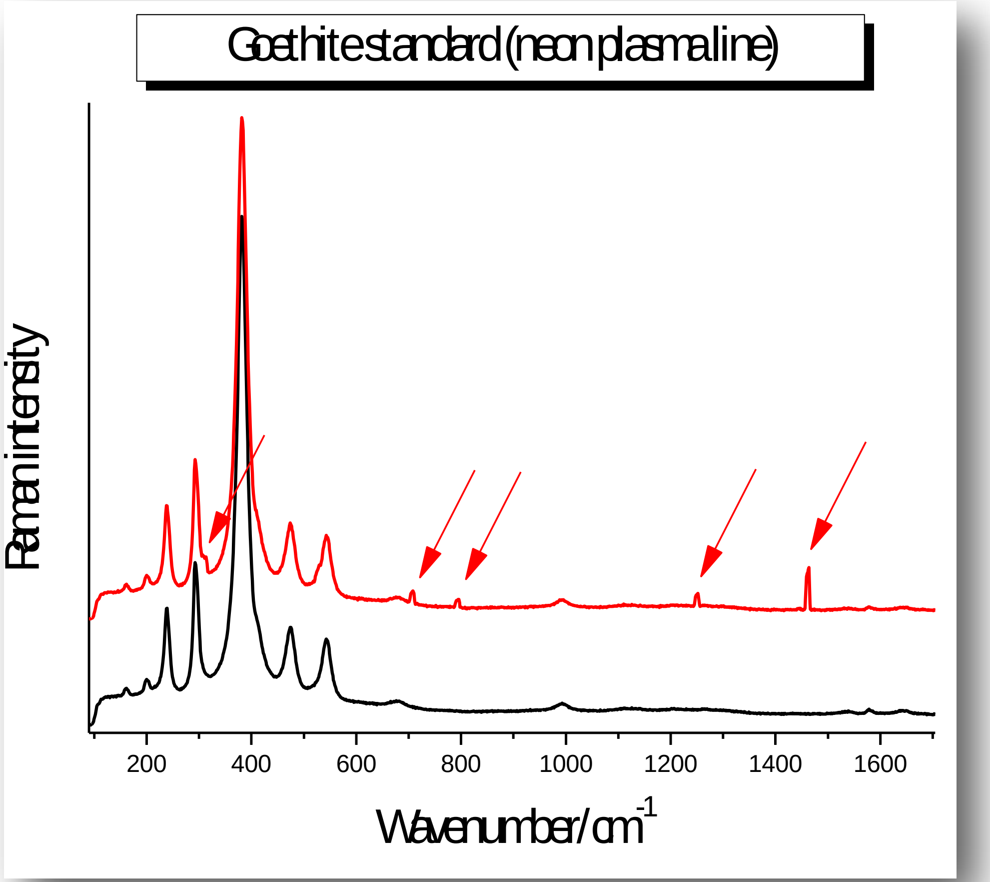


M. Miyazaki et al., *Dental Materials*, **19** (3), 2003, pp. 245–251

Ad-hoc calibration

Neon plasma lines (red lasers)

Mercury line at 1122 cm-1 (514.5 nm)



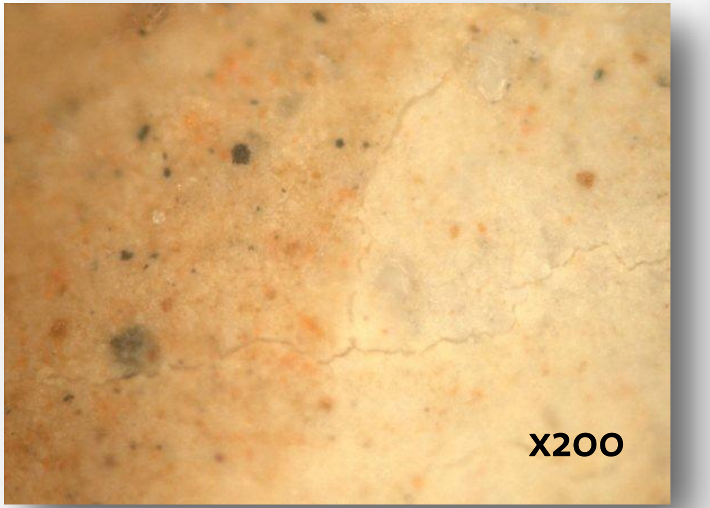
Calibrating Raman Spectrometers Using a Neon Lamp
S. B. Kim, R. M. Hammaker, and W. G. Fateley

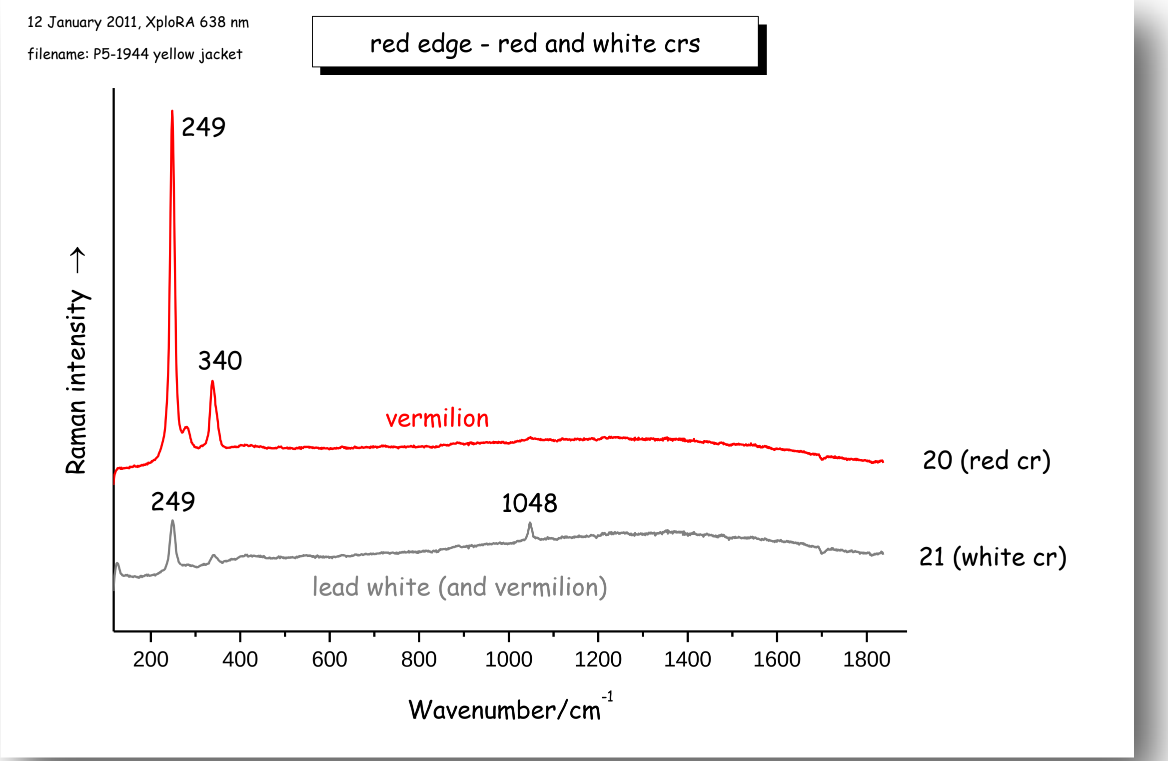
Applied Spectroscopy, Vol. 40, Issue 3, pp. 412-415 (1986)

Problems

Interference

Strong scatterer + weak scatterer

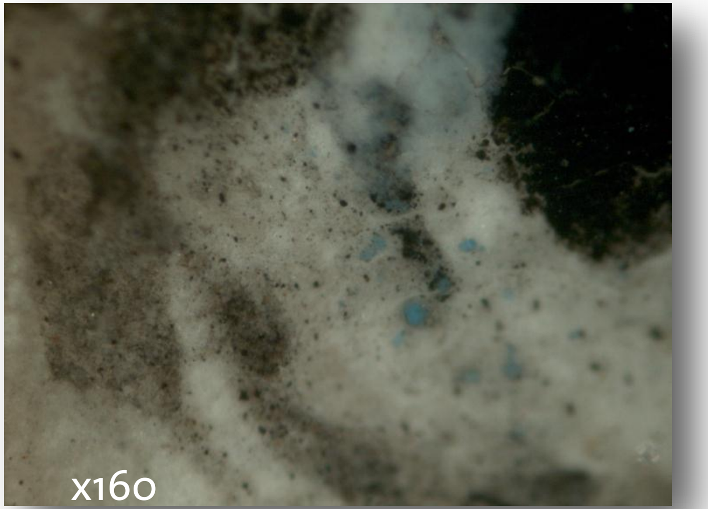


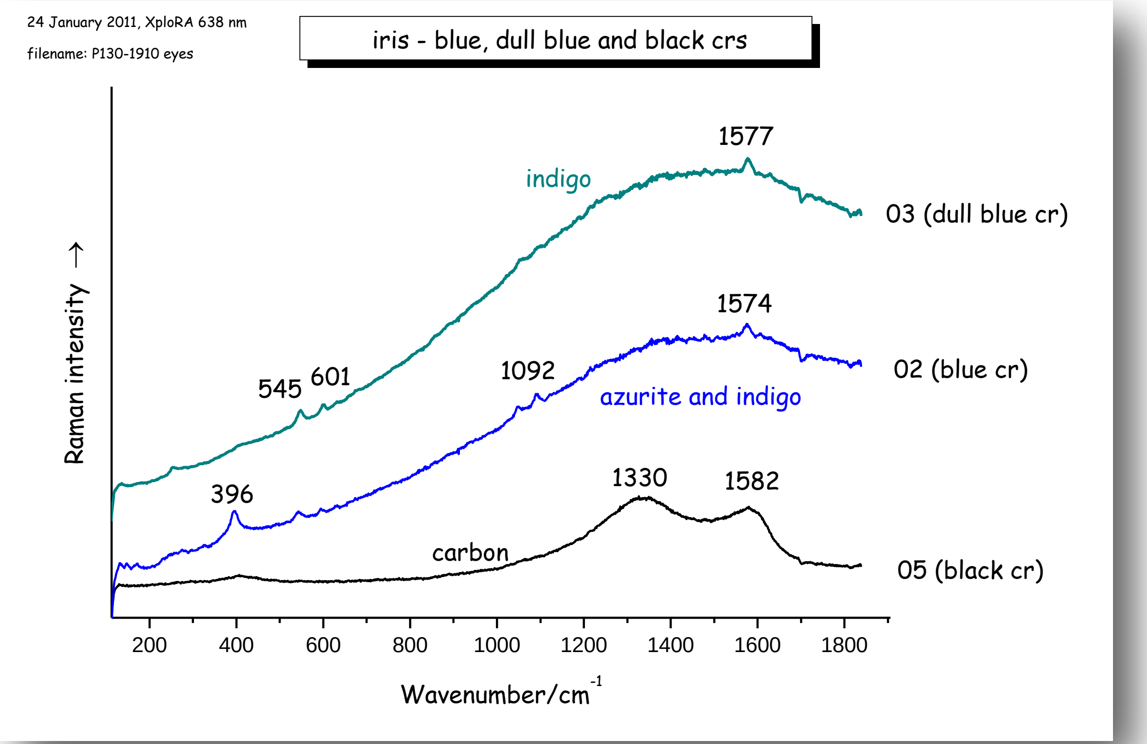


Problems

Interference

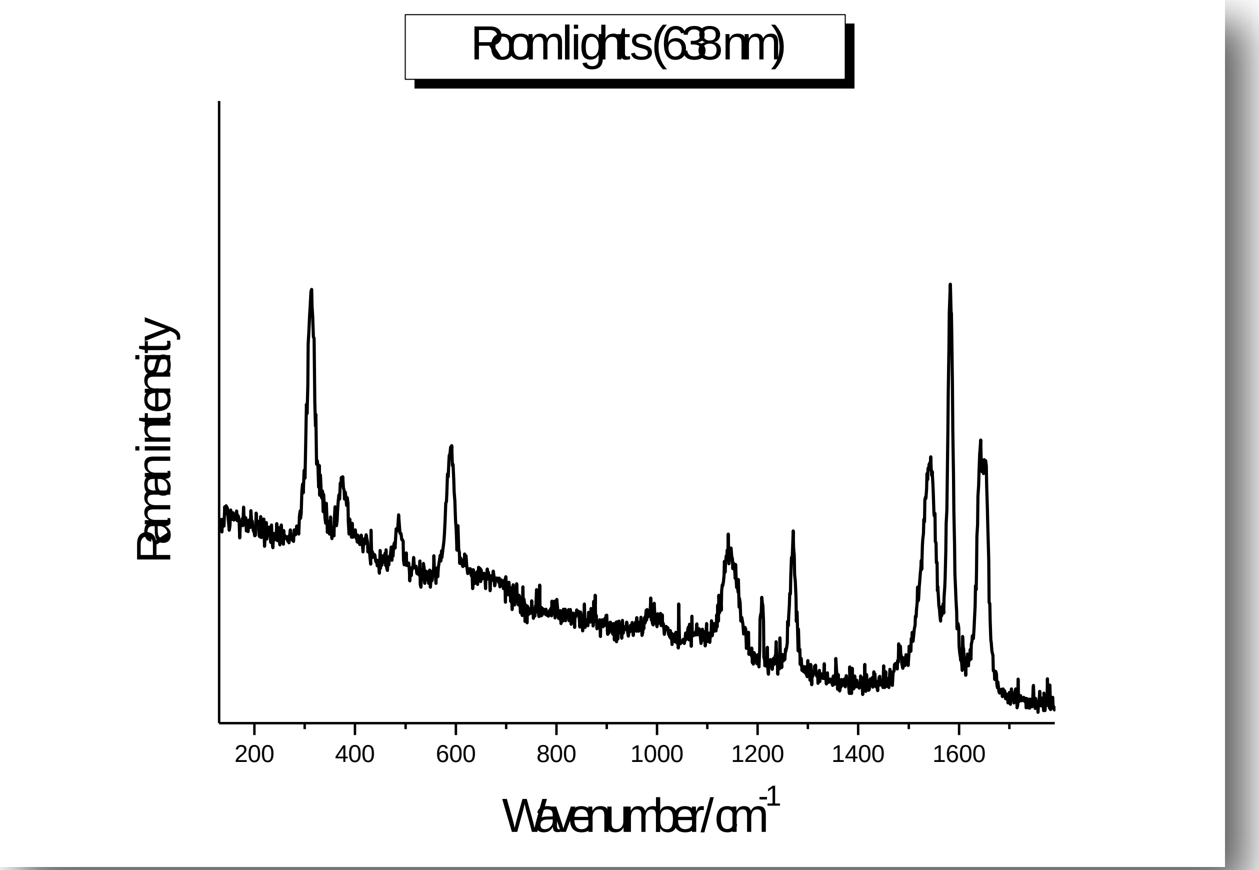
Weak scatterer + weak scatterer





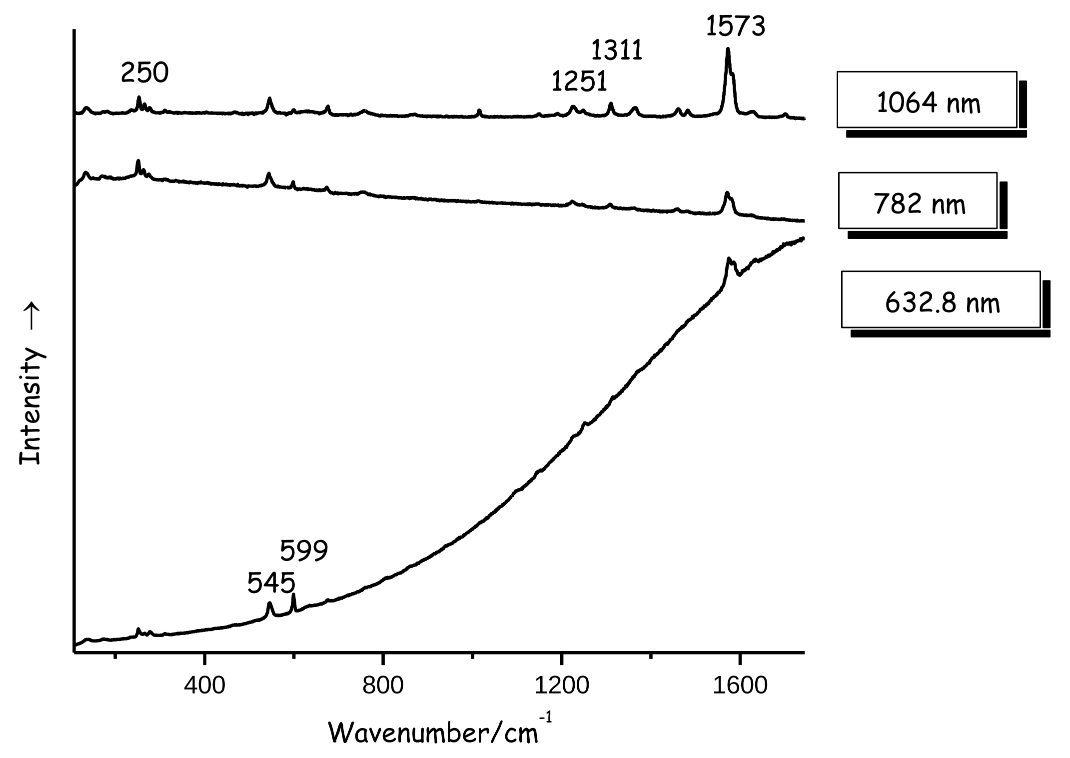
Problems

Room lights



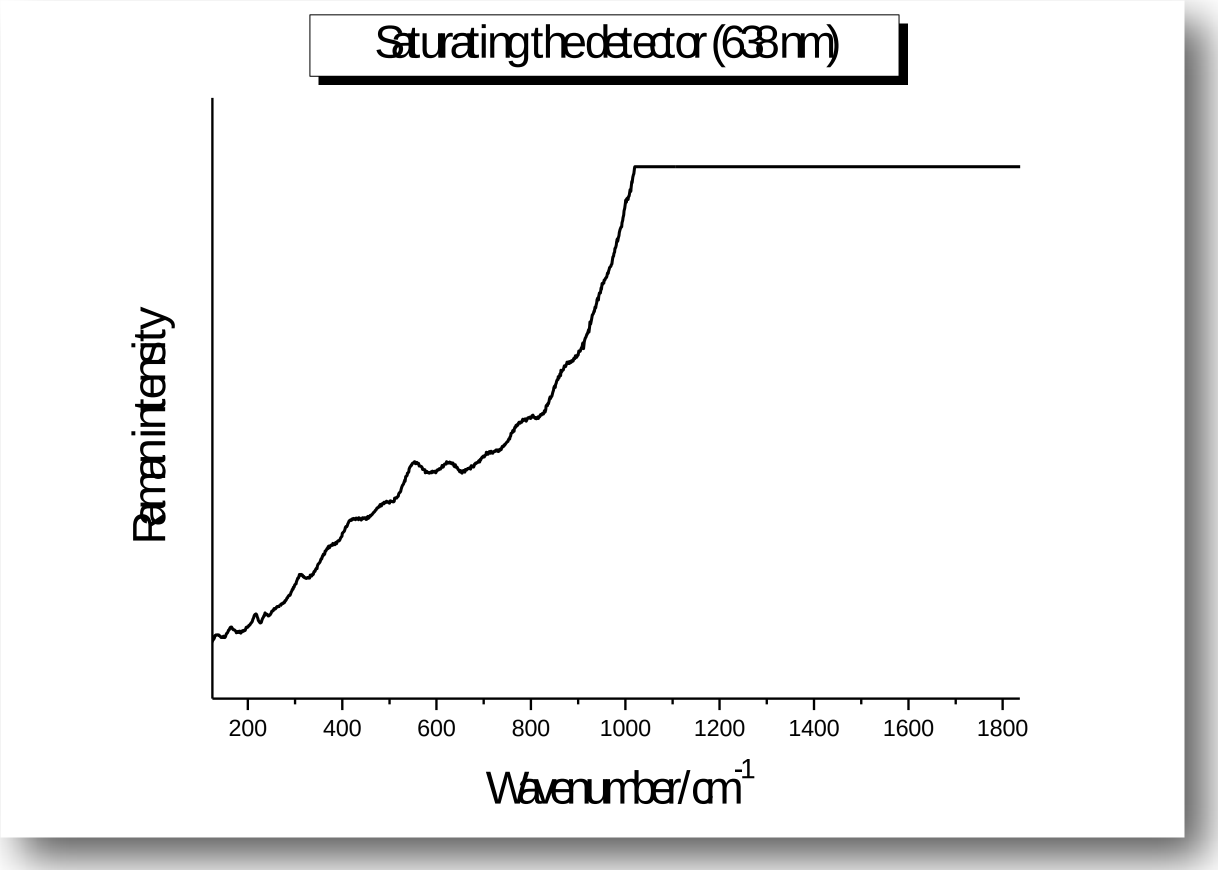
Problems

Fluorescence



Problems

Fluorescence



Change wavelength!!!

Problems

Fluorescence

- Change wavelength
- Lower the power at the sample
- Lower the accumulation time
- Defocus laser
- Accept reality: your sample is not collaborating

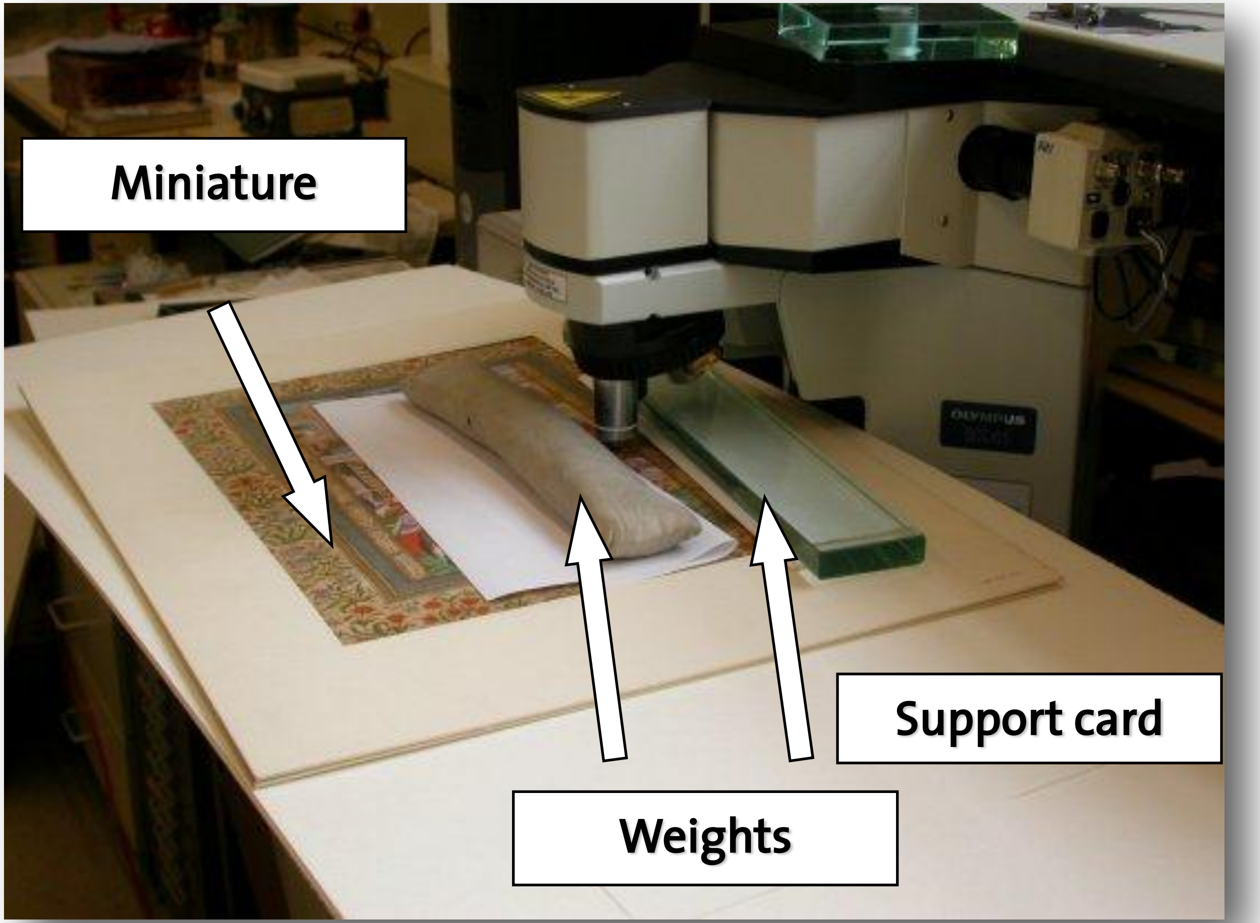
Problems

Stability and focussing issues

Natural vibrations

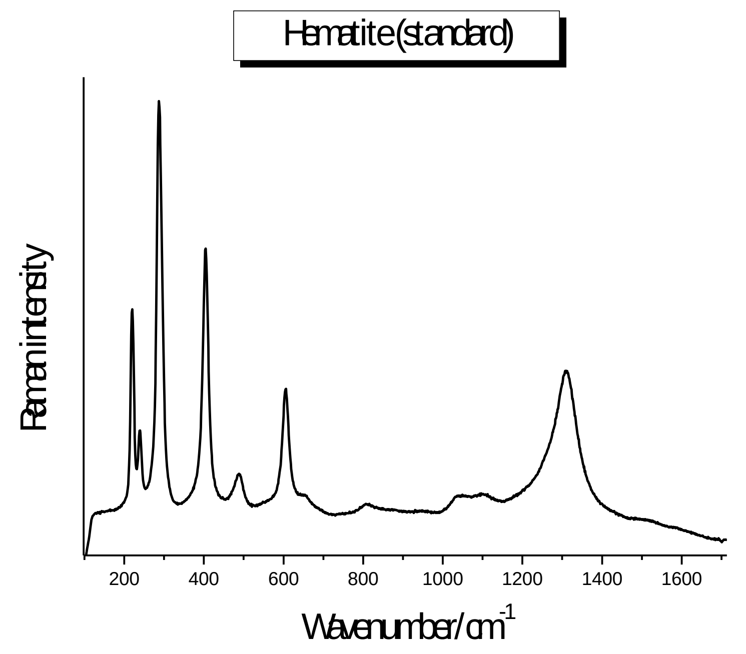
Man-made vibrations

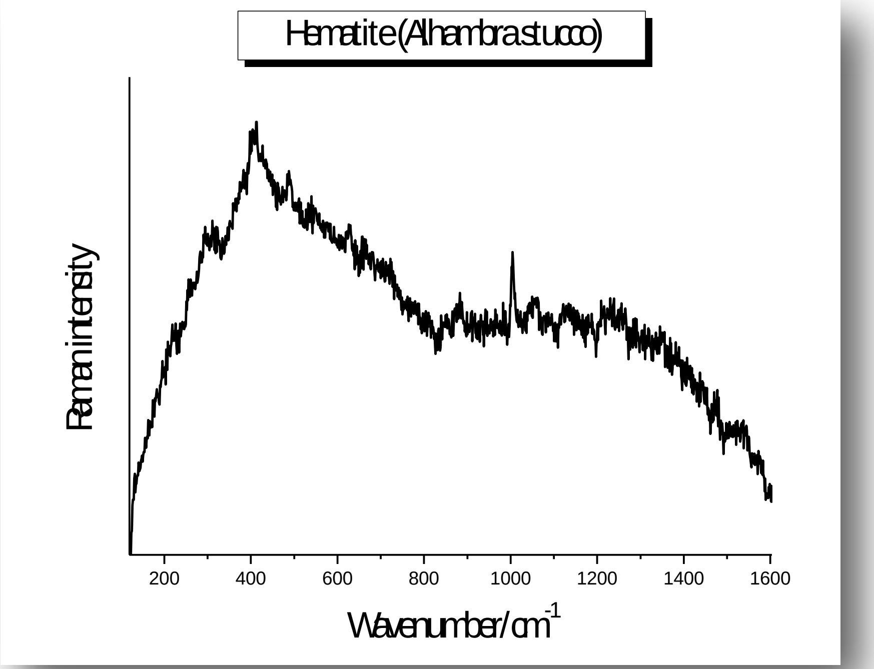
Use weights



Raman spectra of pigments: theory and real life

Never expect spectra like those shown in libraries or reference collections!!!

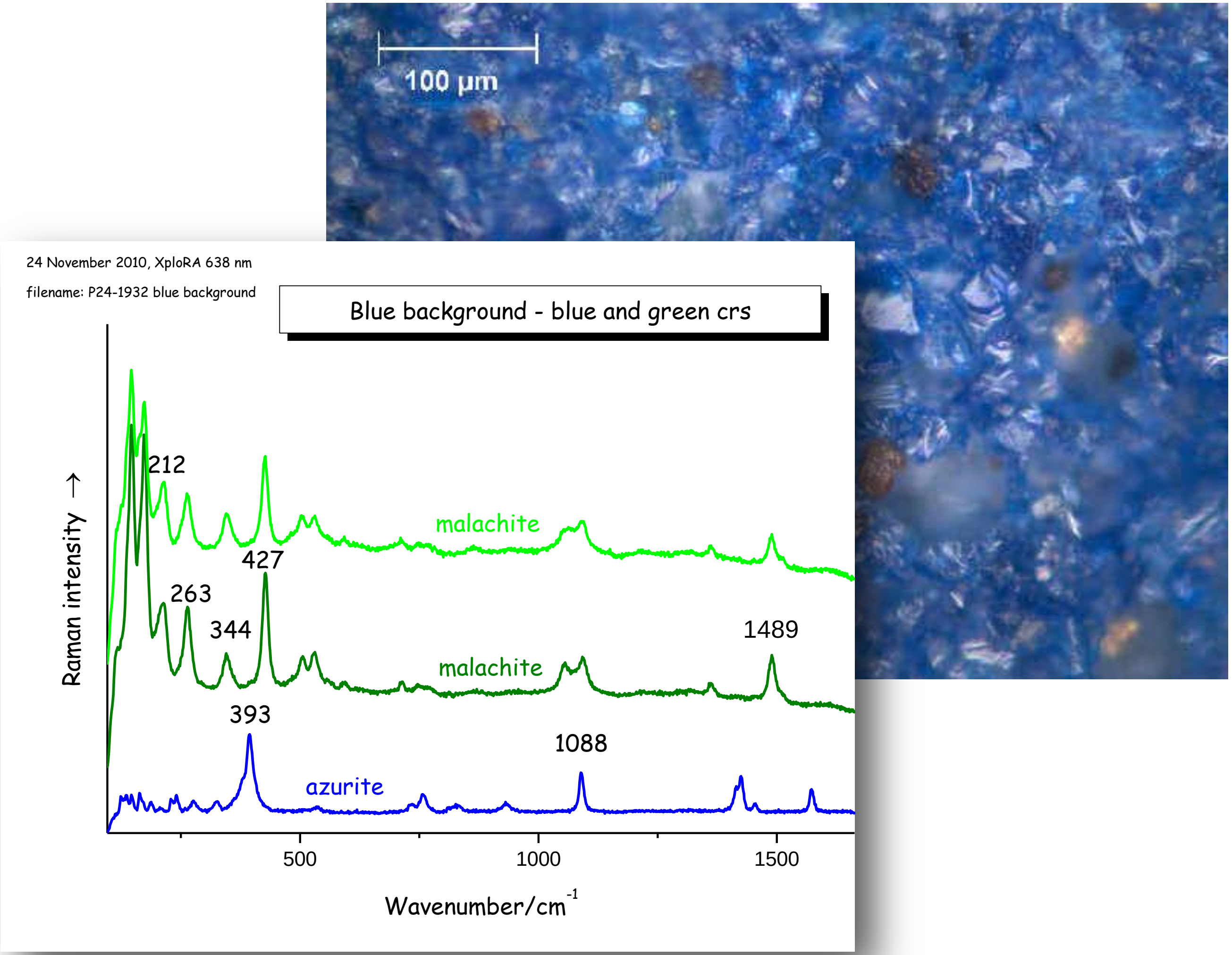




Many contaminants can also be present: interference!

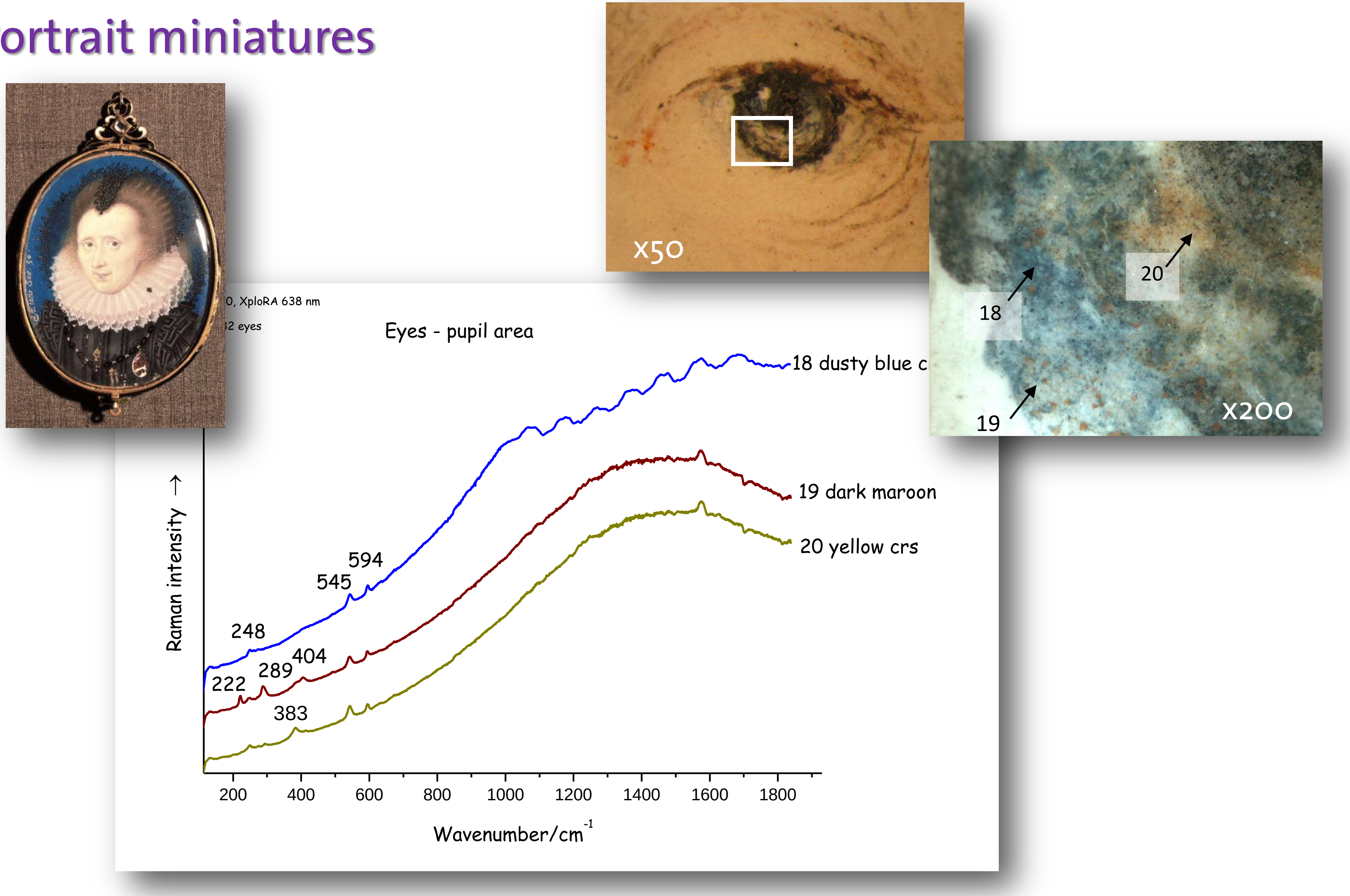
Case studies

Portrait miniatures



Case studies

Portrait miniatures



Case studies

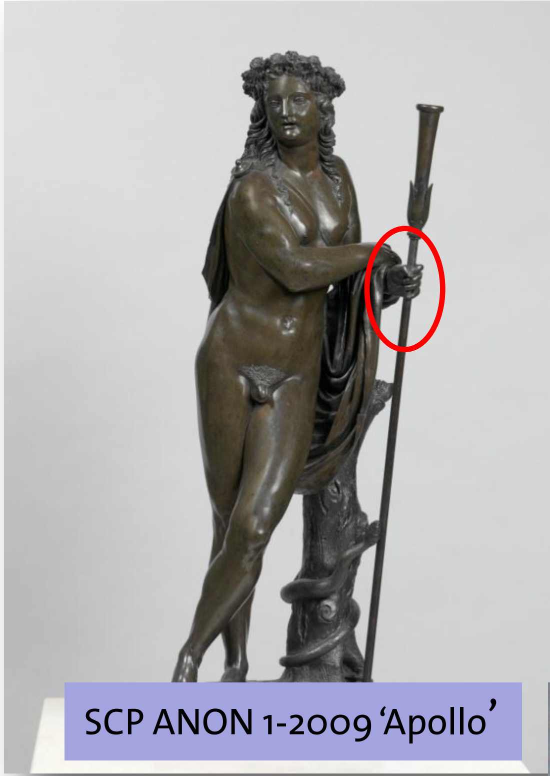
Watercolours (prints)

Khalighat painting

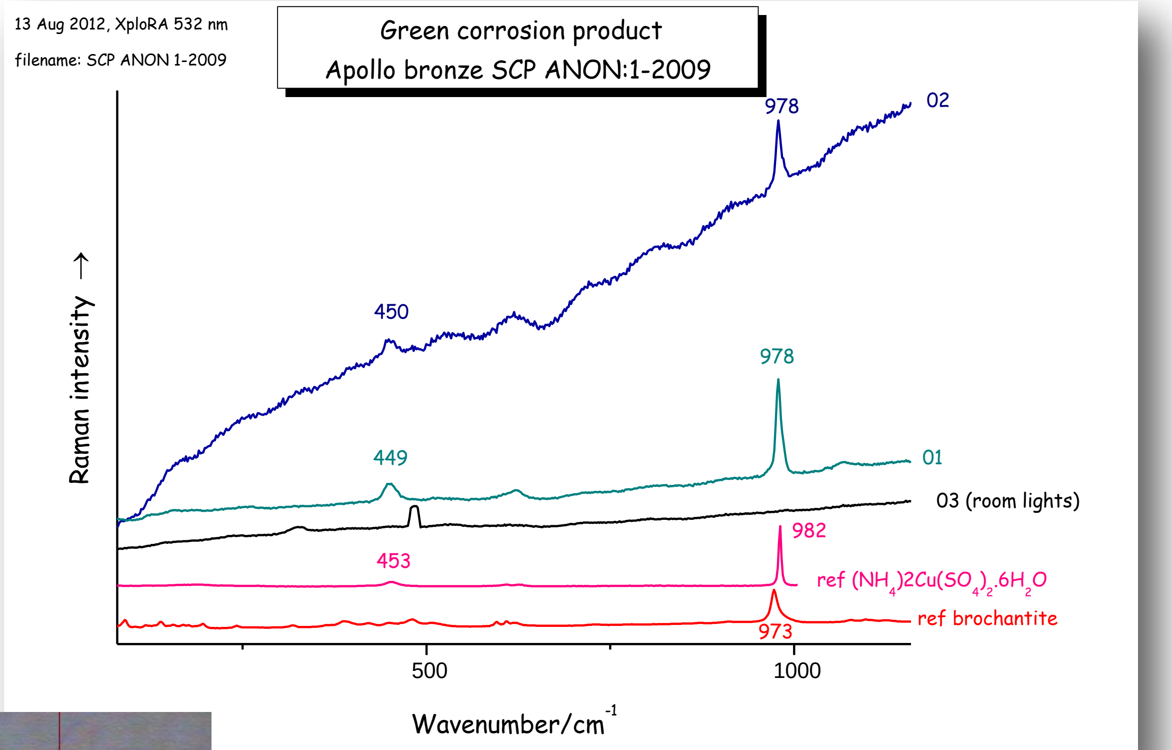
- Fluorescence (medium)
- Small particle size
- Organic dyes

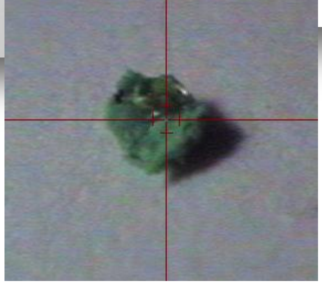
Case studies

Corrosion products



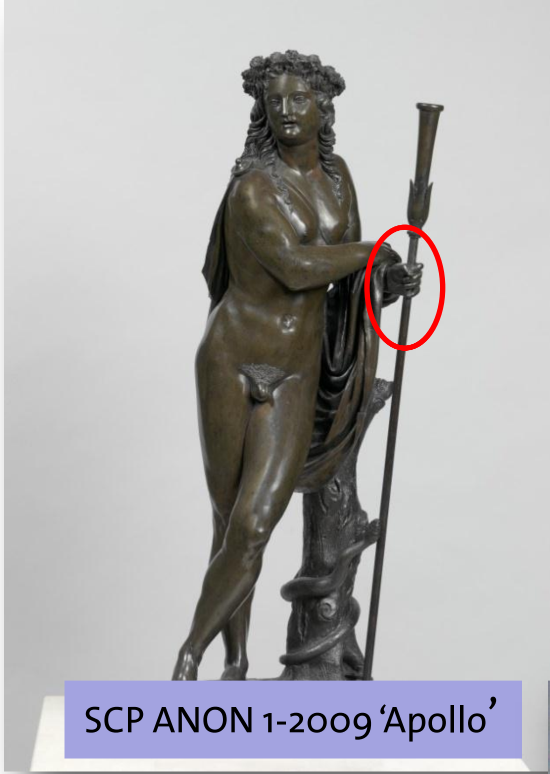
SCP ANON 1-2009 'Apollo'



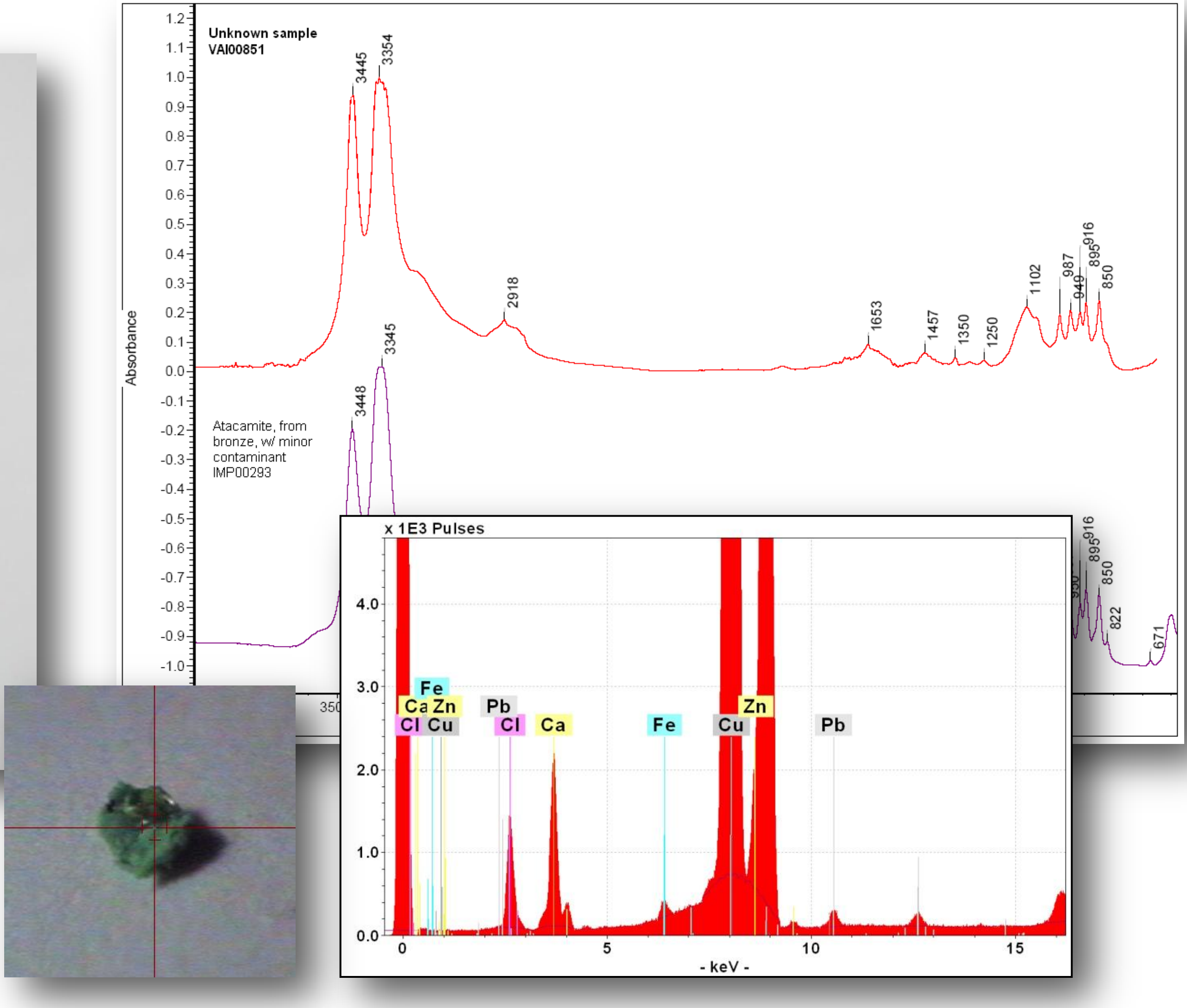


Case studies

Corrosion products



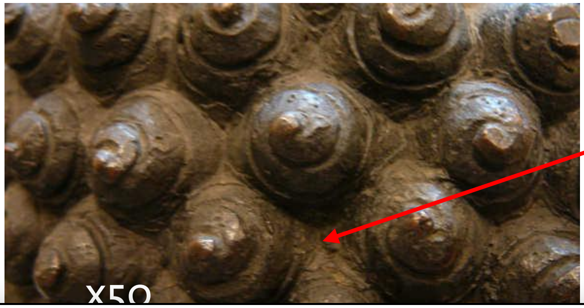
SCP ANON 1-2009 'Apollo'



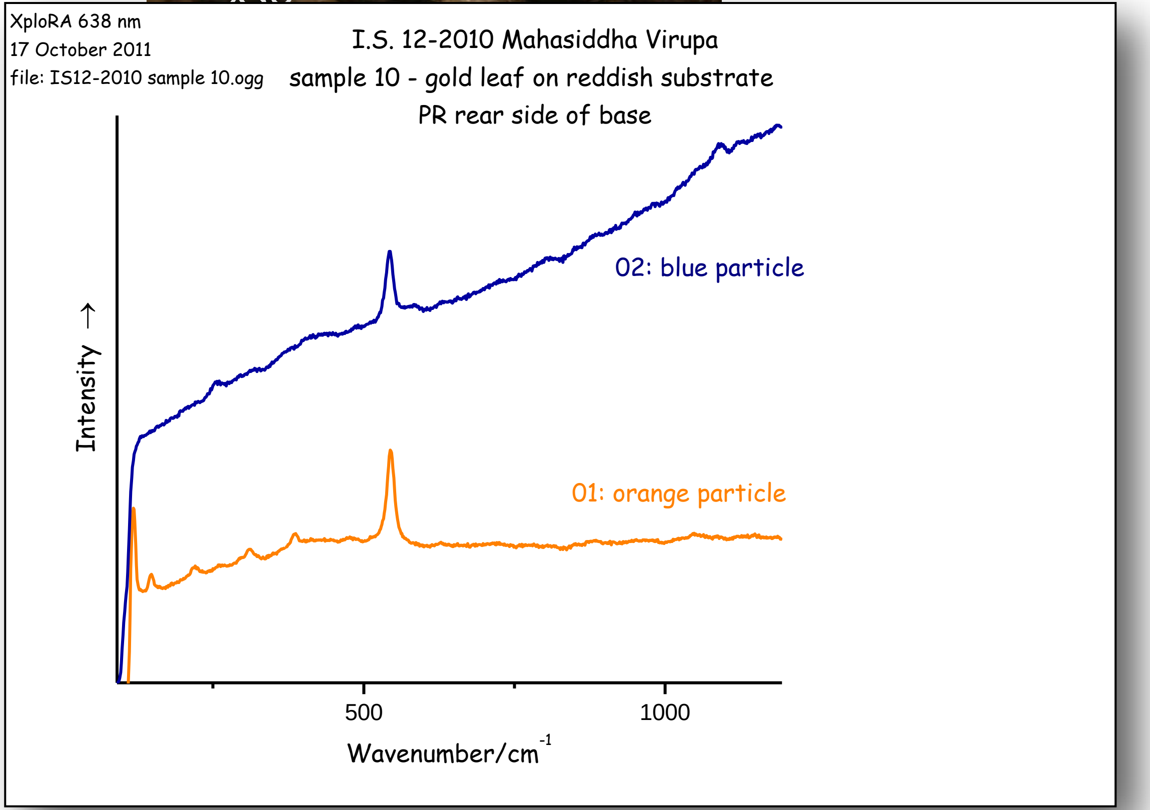
Case studies

Miscellanea

Mahasiddha Virupa (IS.12-2010)

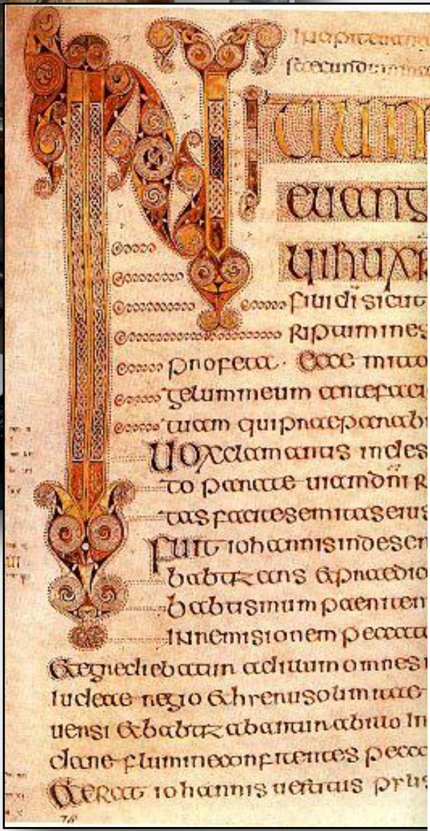


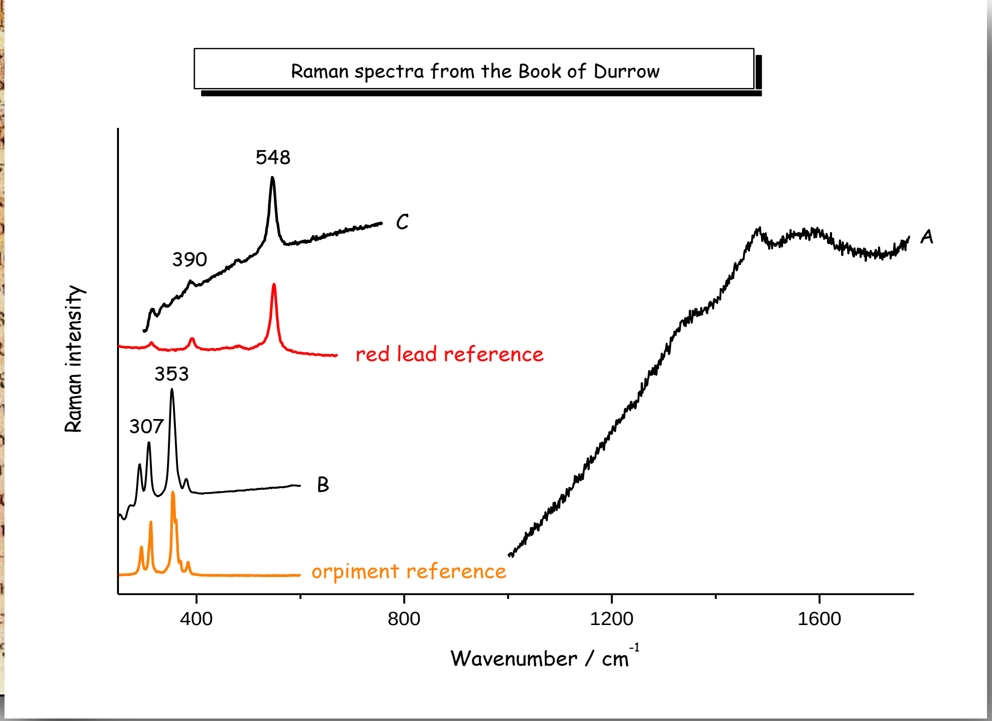
Sample taken from crust for cross section



Case studies

Use of probe

- Stability
- Fluorescence
- Spatial resolution

Book of Durrow, Trinity College Dublin



Other limitations

- Size and location on object
- Not too good for binding media
- Not good for light-absorbing materials (risk of laser-induced degradation)
- Always choose your excitation wavelength carefully

Conclusions

- Raman microscopy is a valuable tool in the analysis of Museum objects
- Fast and reliable, albeit with some drawbacks
- New special attachments can widen the range of objects
- Can assist in routine analyses as well as in the dating and authentication of objects
- Useful conservation tool (degradation studies)
- Complementary techniques may be needed

Acknowledgements

- Mariafrancesca Aru, Lynn Chua, Soraya Alcalà, Vera Lopez-Roca Balanzà, Anna Cesaratto, Michelle Shulman, Richard Hark and Katie Houston.

- IRUG

- V&A curators and conservators

- Greg Smith, Karen Trentelman, HORIBA, Renishaw, Bruker

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see also http://www.chem.ucl.ac.uk/resources/raman/index.html

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[4] D. Bersani, P. P. Lottici, *Anal.Bioanal.Chem,* **397**, 2631, **2010**.

[5] G.D. Smith, R.J.H. Clark, Raman microscopy in art history and conservation science, *Reviews in Conservation*, 2, **2001**.

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[1] R. D. Harley, *Artists' Pigments, c. 1600–1835: A Study in English Documentary Sources*, Butterworth, London, **1970.**

[2] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *The Pigment Compendium: A Dictionary of Historical Pigments*, Elsevier, London, **2004.**

[3] R.L. Feller (Ed.), *Artists' Pigments, A Handbook of their History and Characteristics,* vol. 1, Cambridge University Press, Cambridge, **1986.**

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Infrared & Raman Users Group

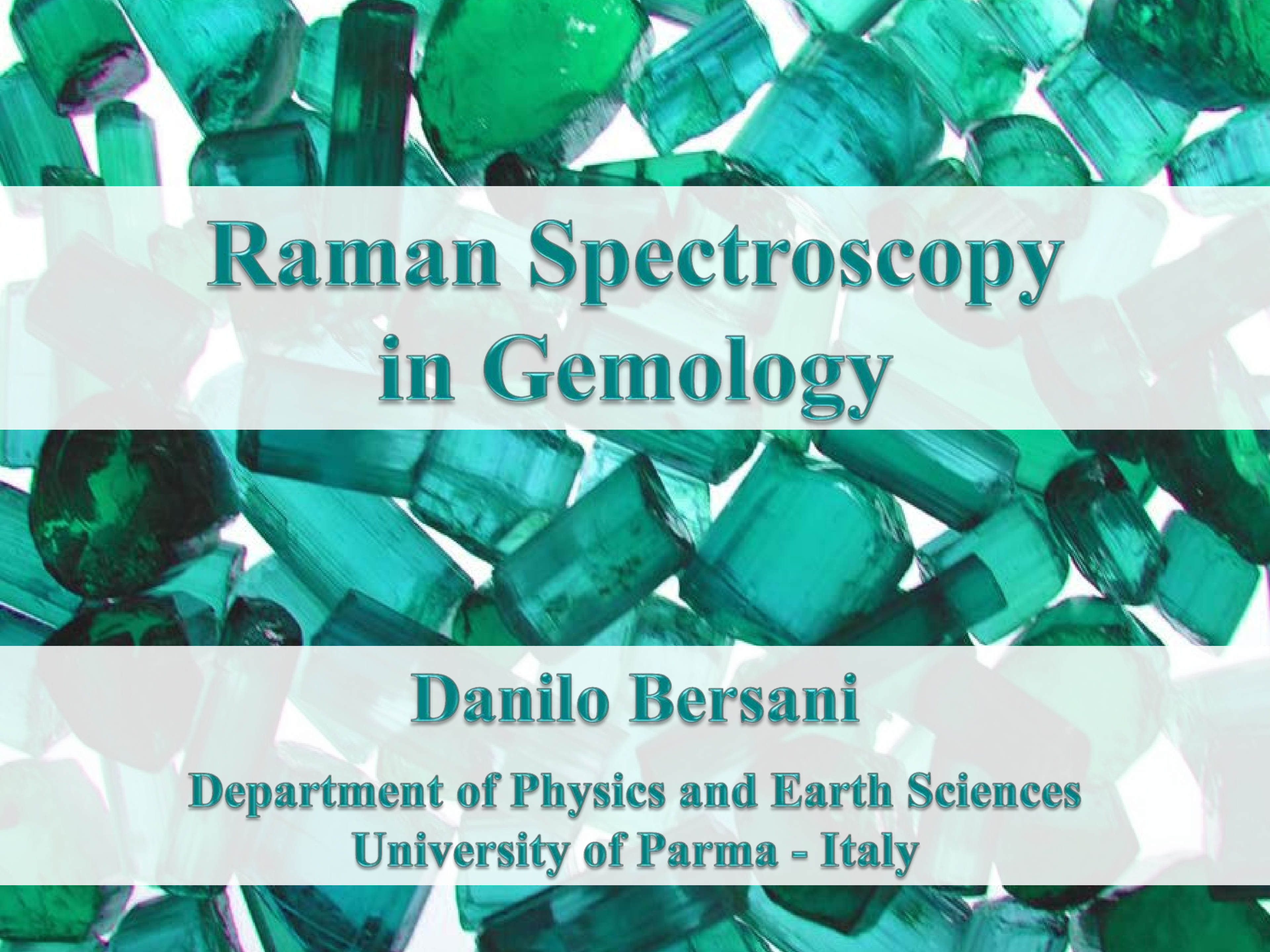
Raman Spectroscopy Workshop

Raman analysis of gems

Danilo Bersani

University of Parma, IT

THURSDAY, SEPTEMBER 27: LECTURE 6



Raman Spectroscopy in Gemology

Danilo Bersani

Department of Physics and Earth Sciences
University of Parma - Italy

Gems and gemological materials in Conservation Science:

1) Hystorical jewels, archaeological objects with stones

2) Contemporary jewels, gemstones

3) Jewelery materials (also organic gems), lapidary

4) Glasses and other simulants

5) Minerals equivalent to gemstones: nearly everywhere in cultural heritage (pigments, ceramics…)

The studied materials

Many gems are well-defined mineral species, such as diamond (C); most gemstones are silicates (beryl, topaz and zircon); the second most represented class is oxides (ruby and sapphire).

Often gemstones are members of an isomorphic series.

Nearly all are crystalline inorganic solids, usually good Raman scatterers.

Not only crystals:

- Organogen materials (amber, corals, pearls)
- Amorphous (glass simulants) or amorphized (by heat treatments)
- Organic fillers; fluid inclusions

Many forms:
the more difficult are gems mounted on historical objects or under glass

The first question:

What’s that???

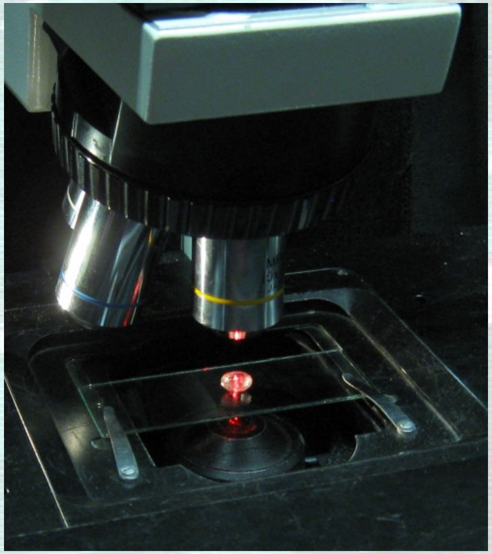
The main question:

How much is it worth????

In a completely non-destructive way!

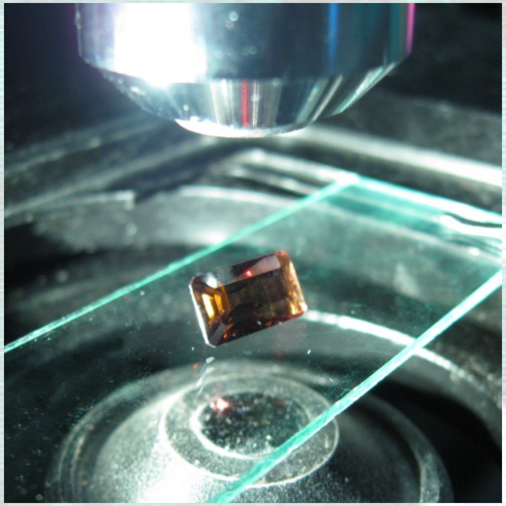
What is required?

- Identification
- Composition
- Natural, synthetic or simulant?
- Provenance
- Genesis
- Purity
- Enhancements



Why Raman and Gems?

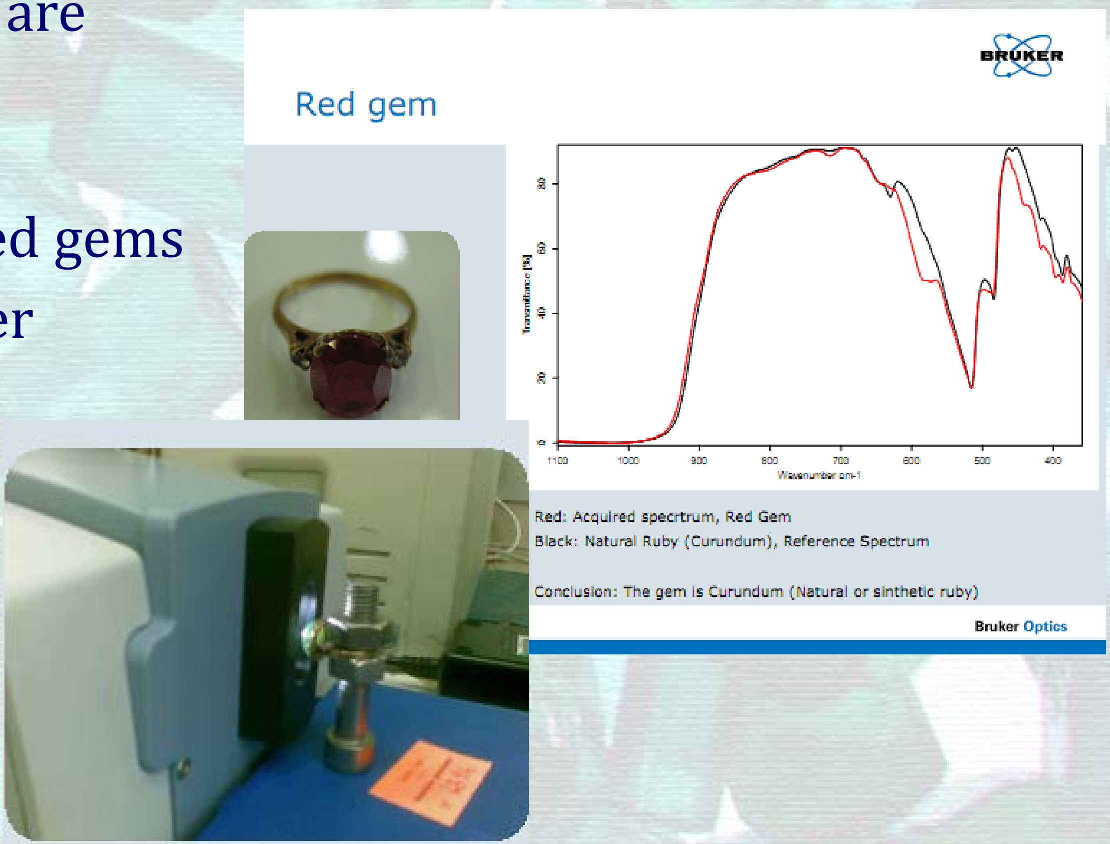
- Non invasive – Contactless
- Quick
- High resolution



Usually gems are studied easily with Raman, due to the non-invasivity of the method, to the presence of clear “fingerprint” features in the spectrum, and the possibility to have extra information thanks to the spacial resolution.

With FTIR only few works are present:

Example: study on mounted gems using alpha-R spectrometer [Diego Sali – Bruker]



Red gem

Red: Acquired specrtrum, Red Gem
Black: Natural Ruby (Curundum), Reference Spectrum

Conclusion: The gem is Curundum (Natural or sinthetic ruby)

Bruker Optics

Our equipment

Jobin-Yvon Horiba LabRam Raman micro-spectrometer

Dispersive (single grating 1800 lines/mm)

Spectral resolution 1-3 cm-1 (depending on the configuration)

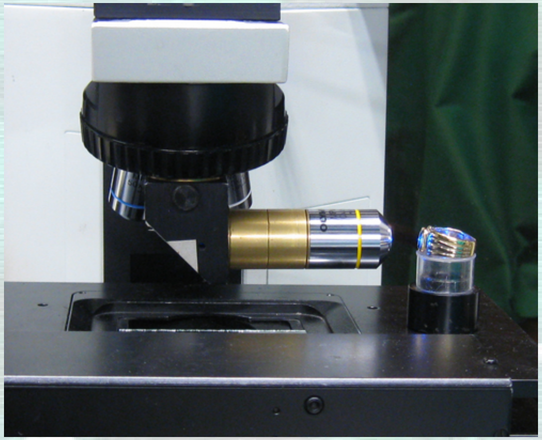
Excitation:

He-Ne Laser 632.8 nm

Doubled solid-state Nd:YAG 473.1 nm
(Laser diode 784.8 nm)

Different sources are required for
RESONANCE and PHOTOLUMINESCENCE
(to measure it and, more often, to avoid it)

- Equipped by CONFOCAL Olympus microscope
- Microscope objectives 10x, 50x, 100x
  + (very important) 50x ULWD
- Spatial resolution 1 μm - micro motorized XY stage
- Linear polarizing filters
- ND filters for power control
  (few thermal problems with gems)

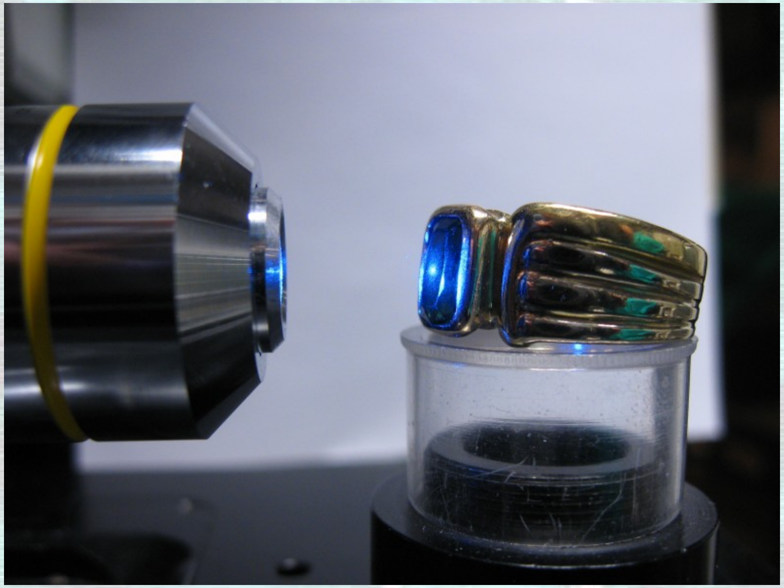


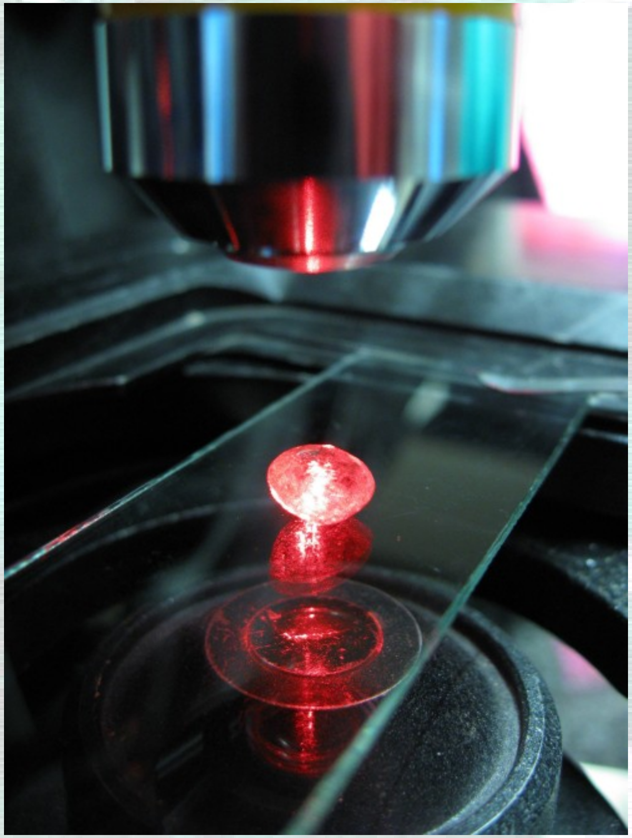
- 90° mirror/prism + tubes for large objects

Fixed or mobile?

Laboratory apparatus:

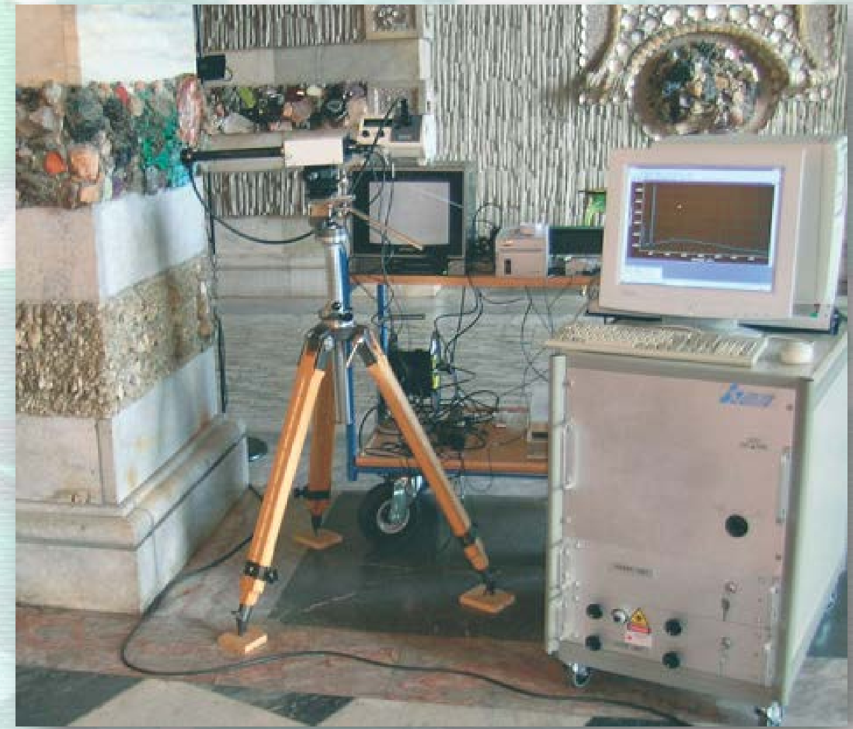
- Space resolution
- Spectral resolution
- Multi-line





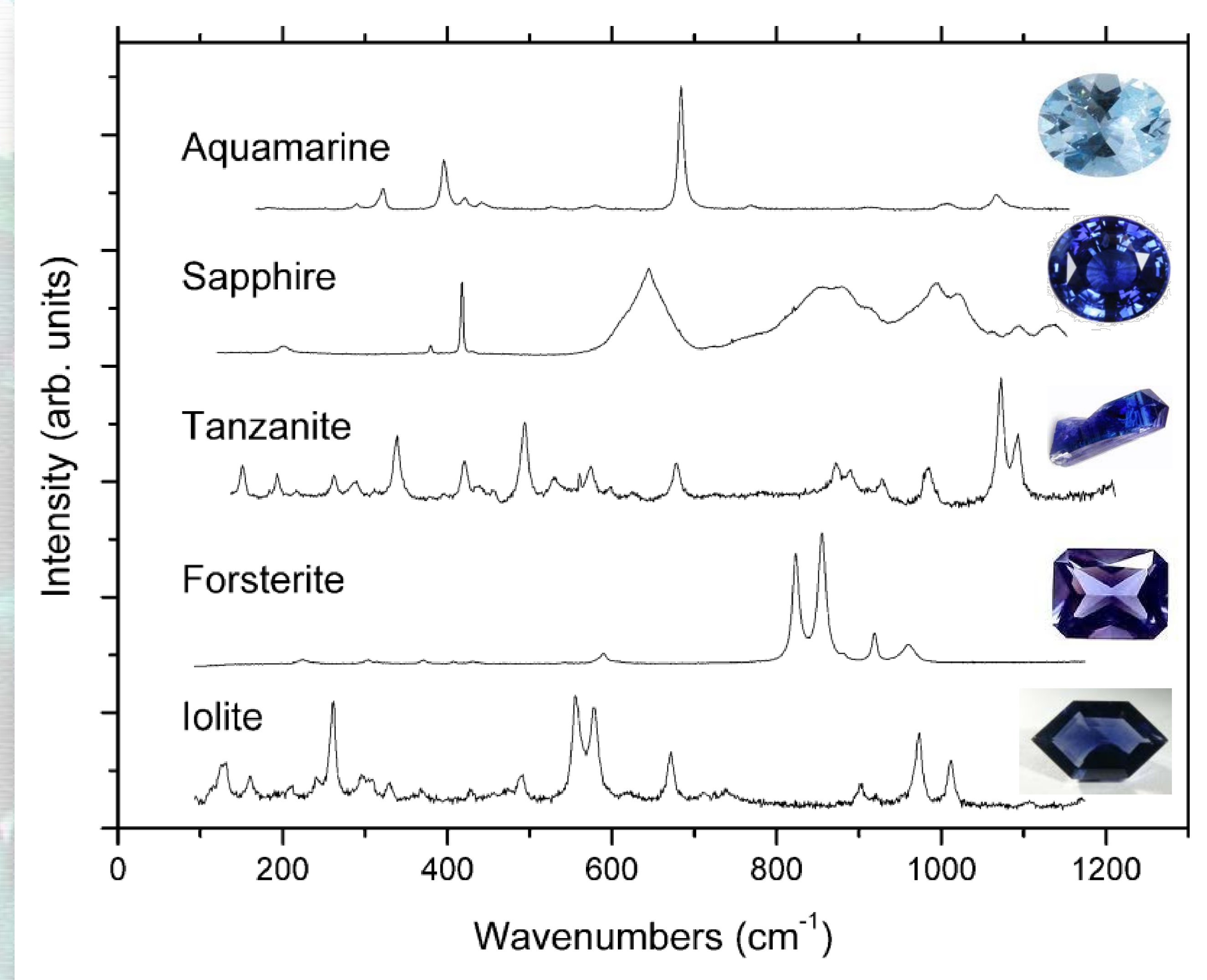
Mobile: fiber optic head

- Museums
- Large objects

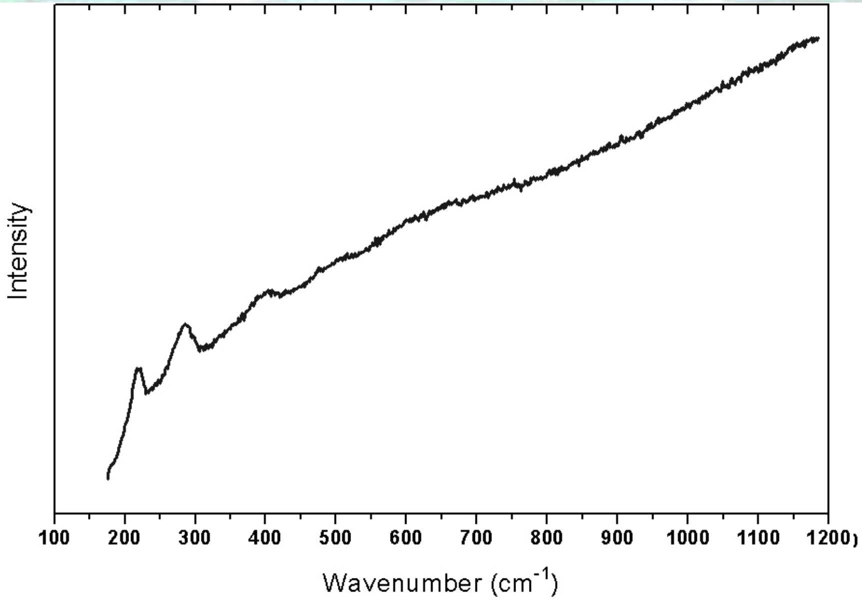


1) IDENTIFICATION

Identification: comparison with references



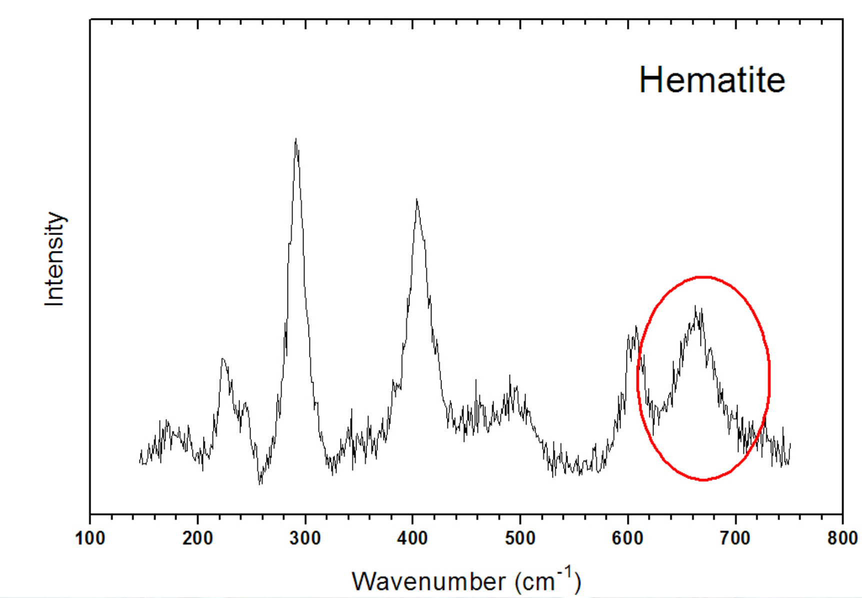
The case of Hematite



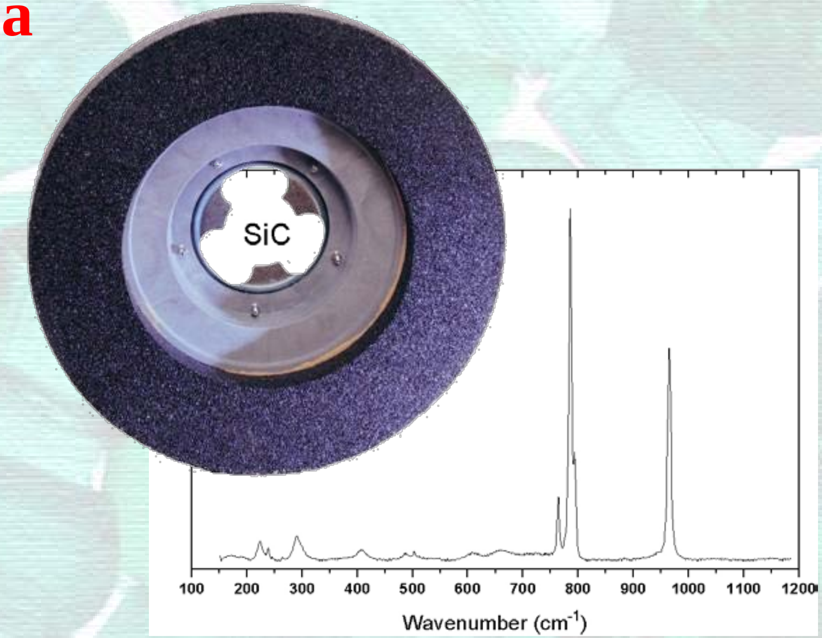
1) Thermal shift and broadening

2) Disorder activated band:

often confused with magnetite residual

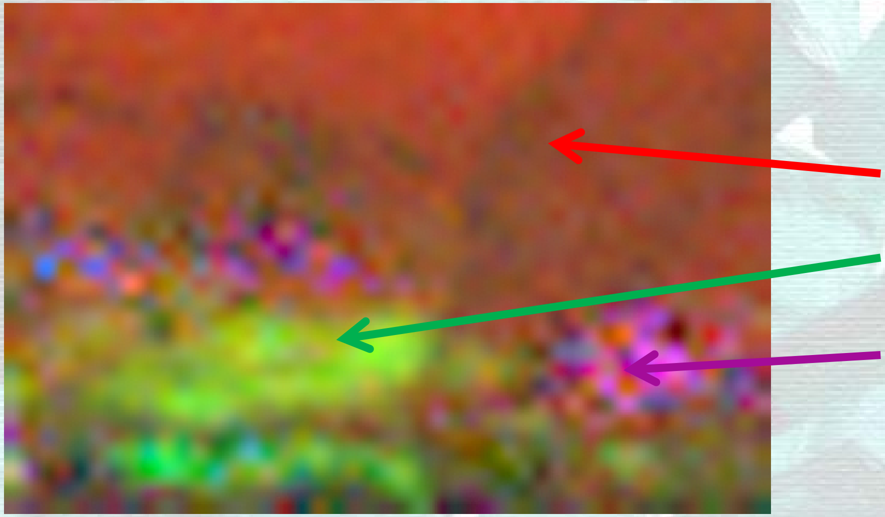


Small impurities with strong spectra



Abrasives and cutting materials

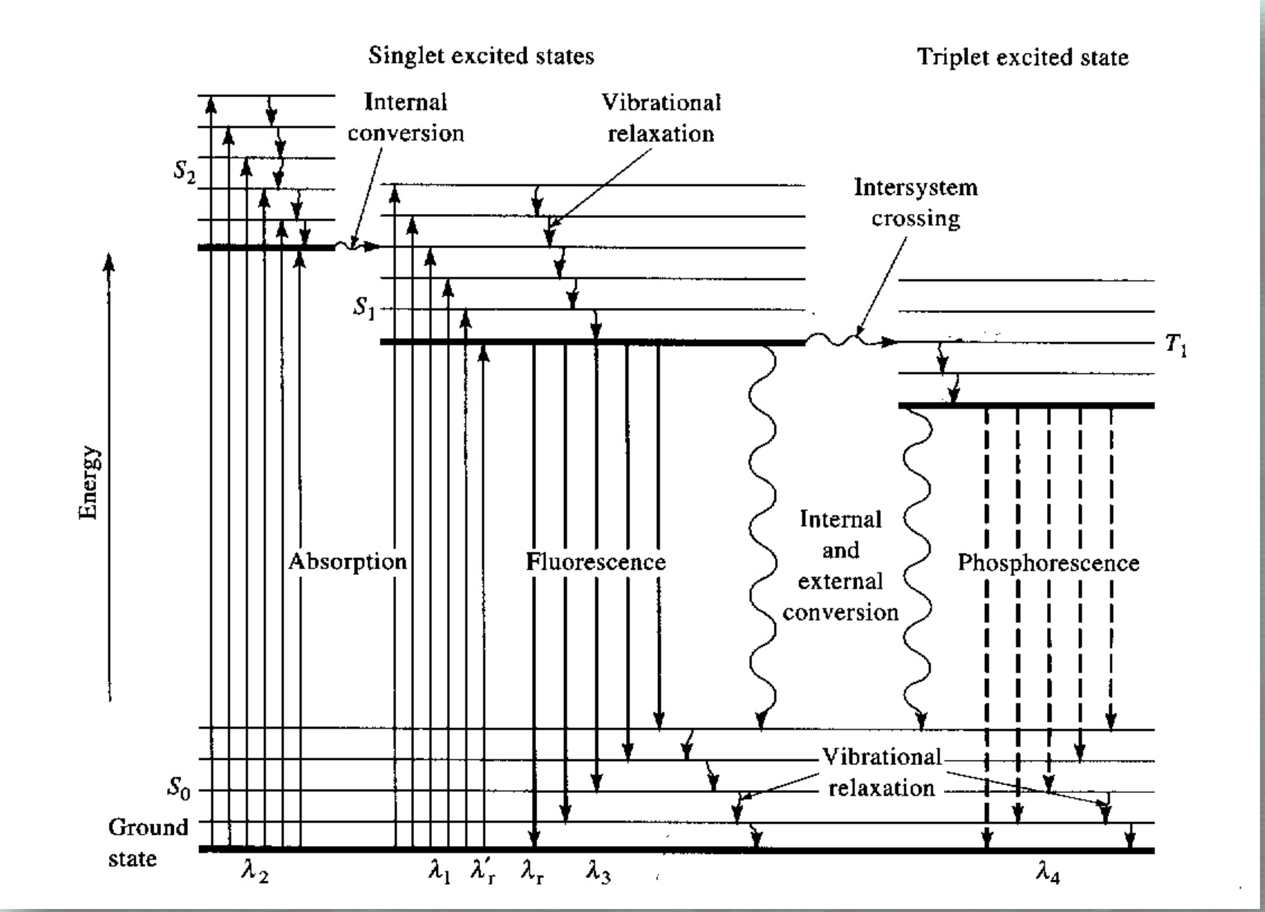
- Silicon Carbide
- Diamond
- Zirconia
- Alumina



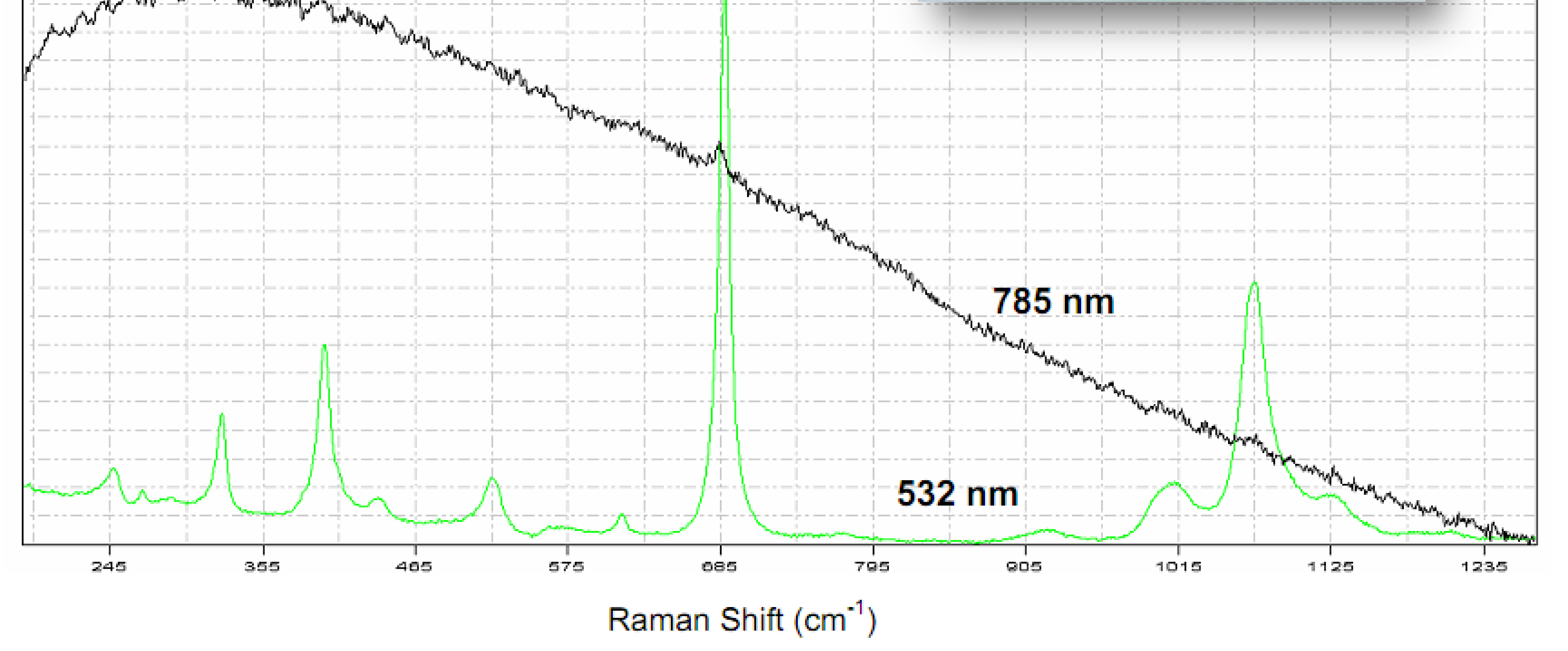
Raman map on a garnet

- Almandine
- Alumina (abrasive)
- Resin

Our enemy fluorescence

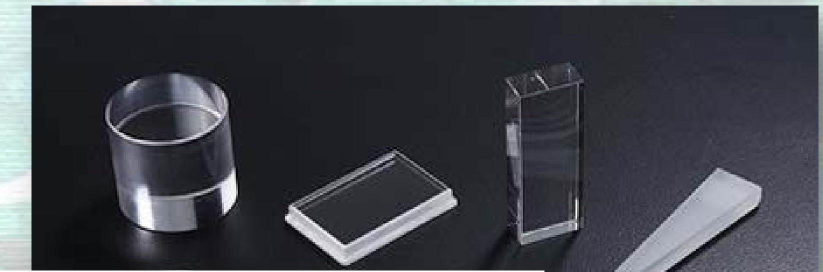


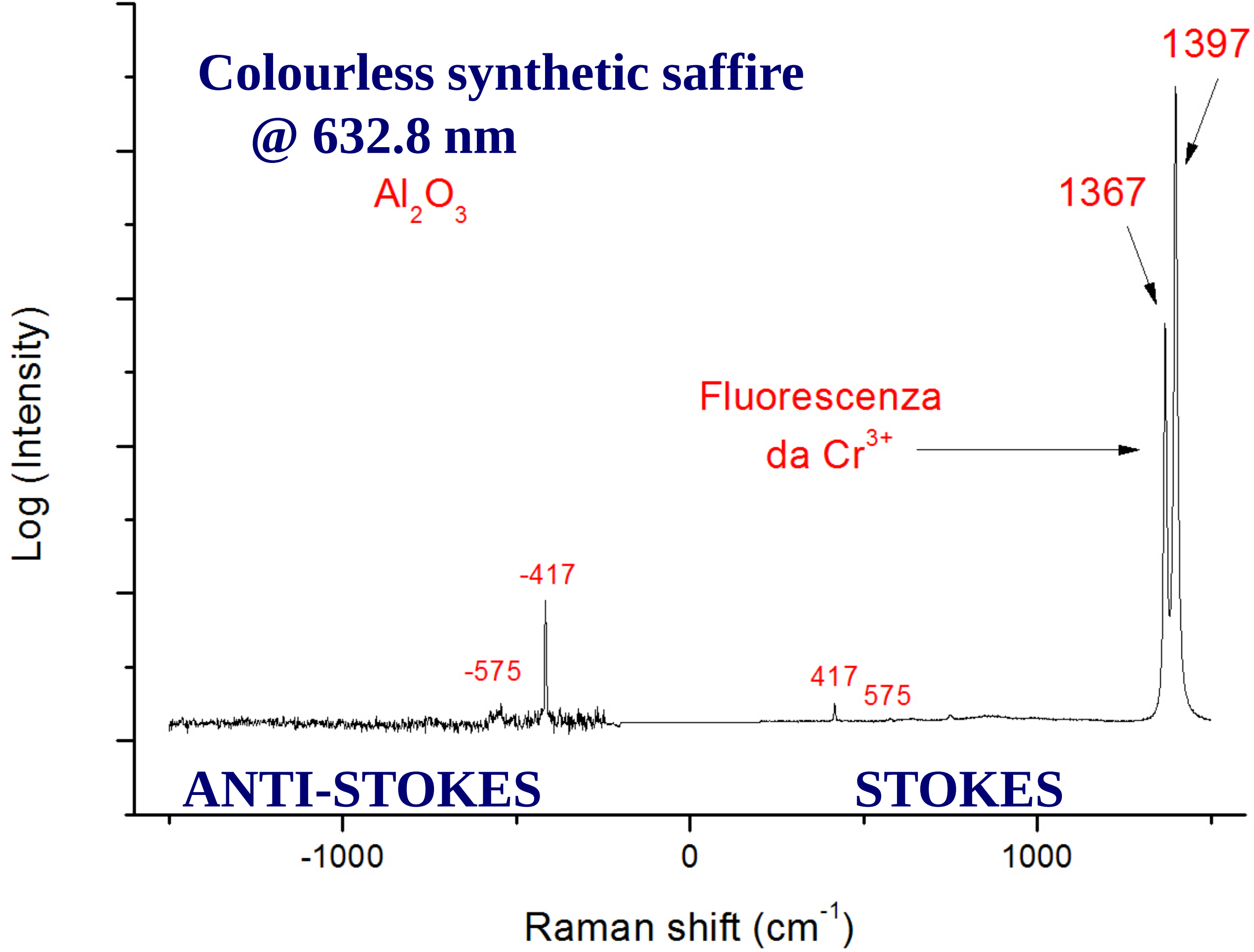
Fluorescence: green beryl



R. Jasinevicius – Thesis -Degree of MASTER OF SCIENCE - THE UNIVERSITY OF ARIZONA 2009

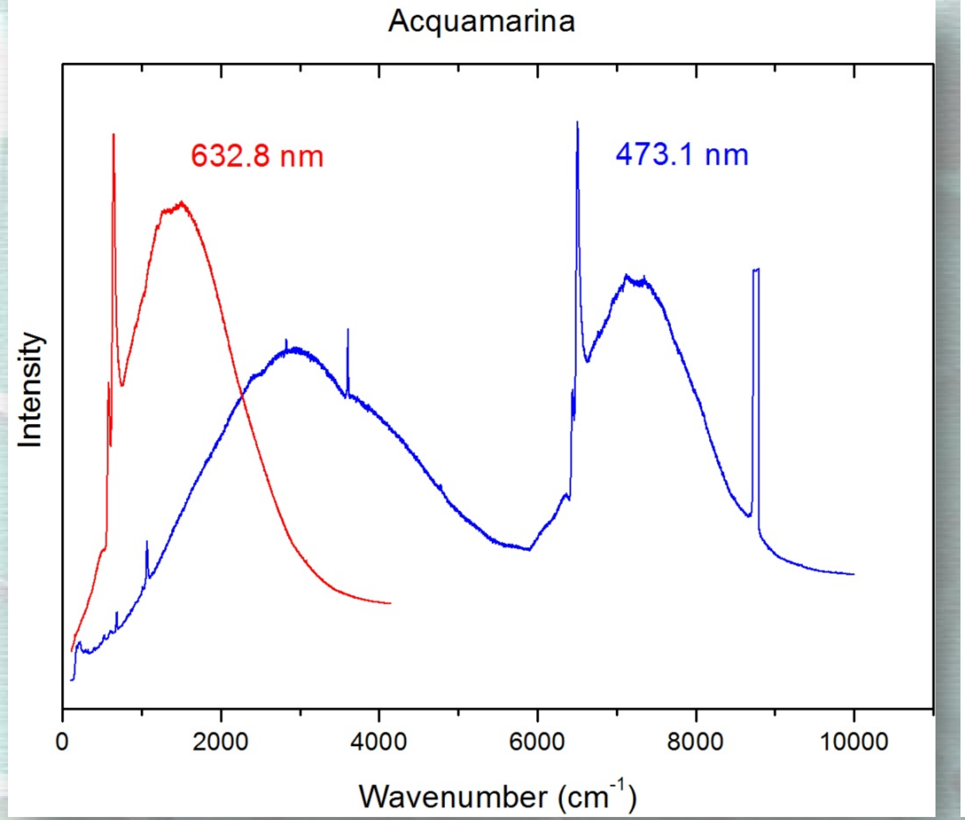
Our friend fluorescence: impurities identification

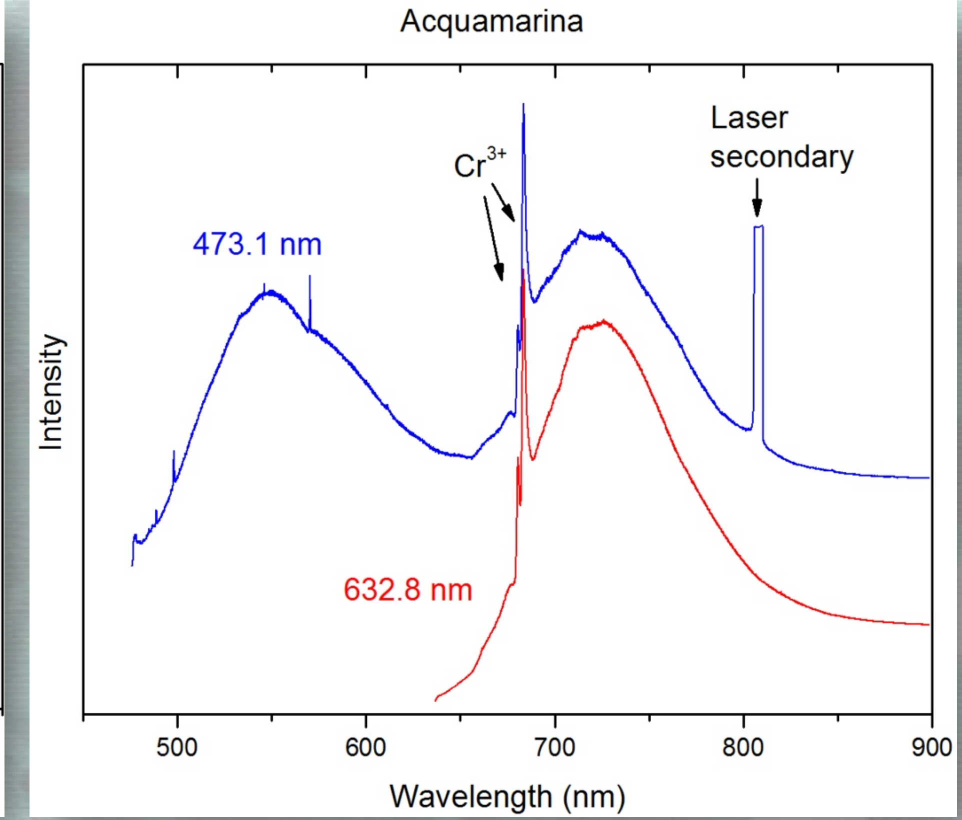




Colourless synthetic saffire @ 632.8 nm

Our friend fluorescence: impurities identification



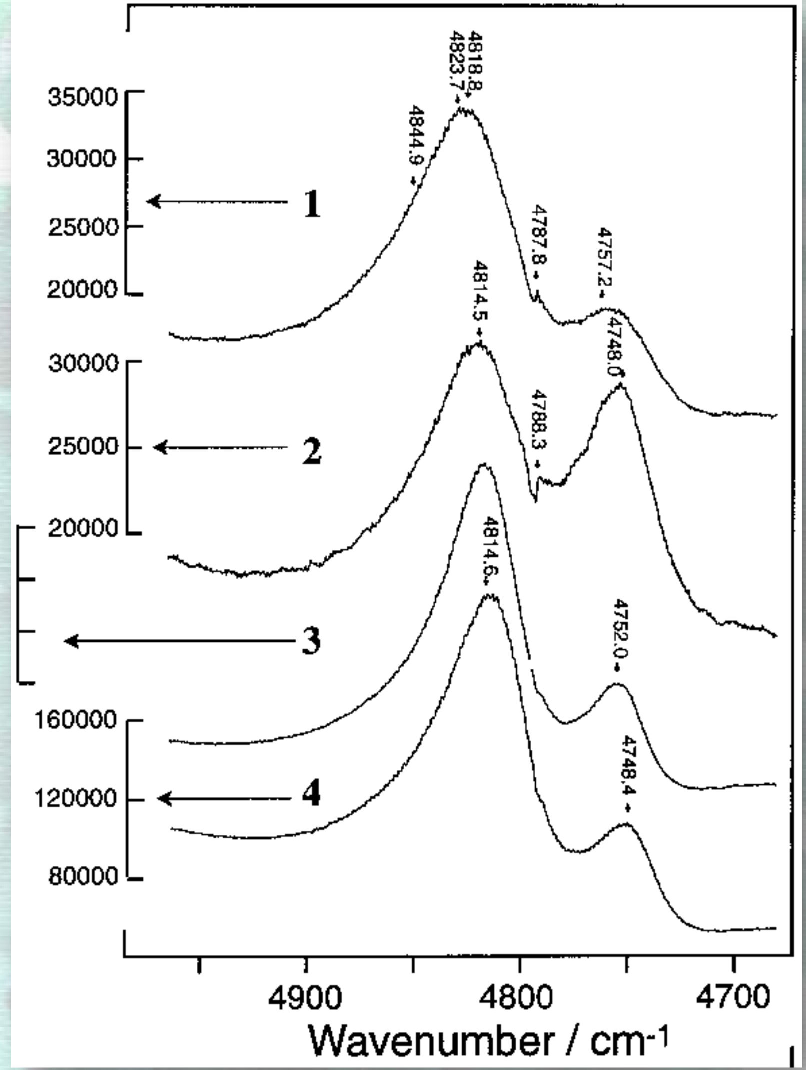


Raman Shift

Wavelength

The position of the PL bands of Cr ions depends on the surrounding atoms.

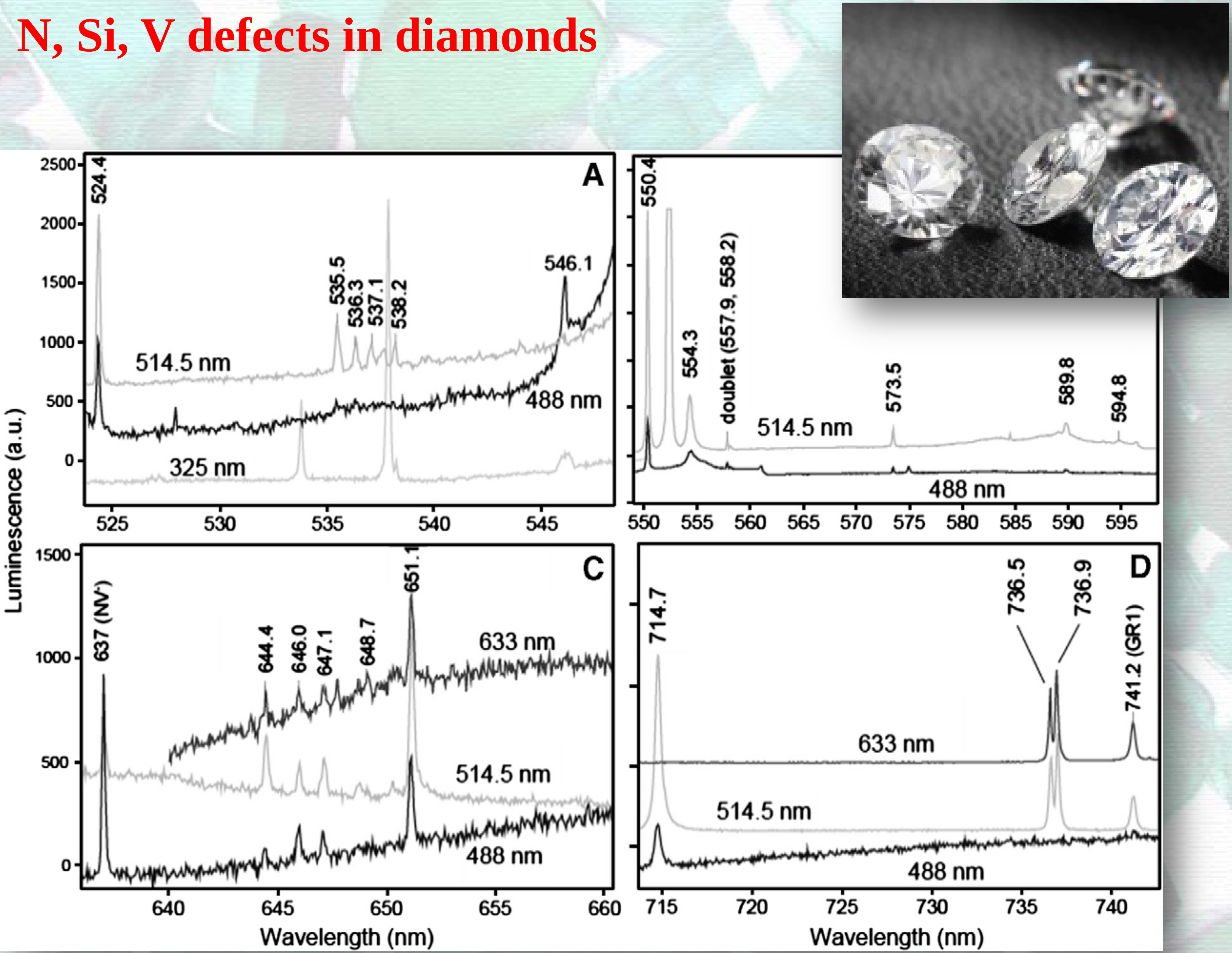
Provenance study on emeralds



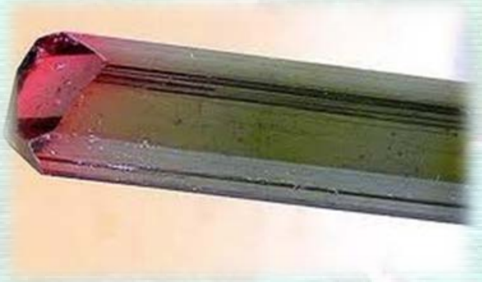
I. Moroz et al. J. Raman Spectrosc. 31, 485–490 (2000)

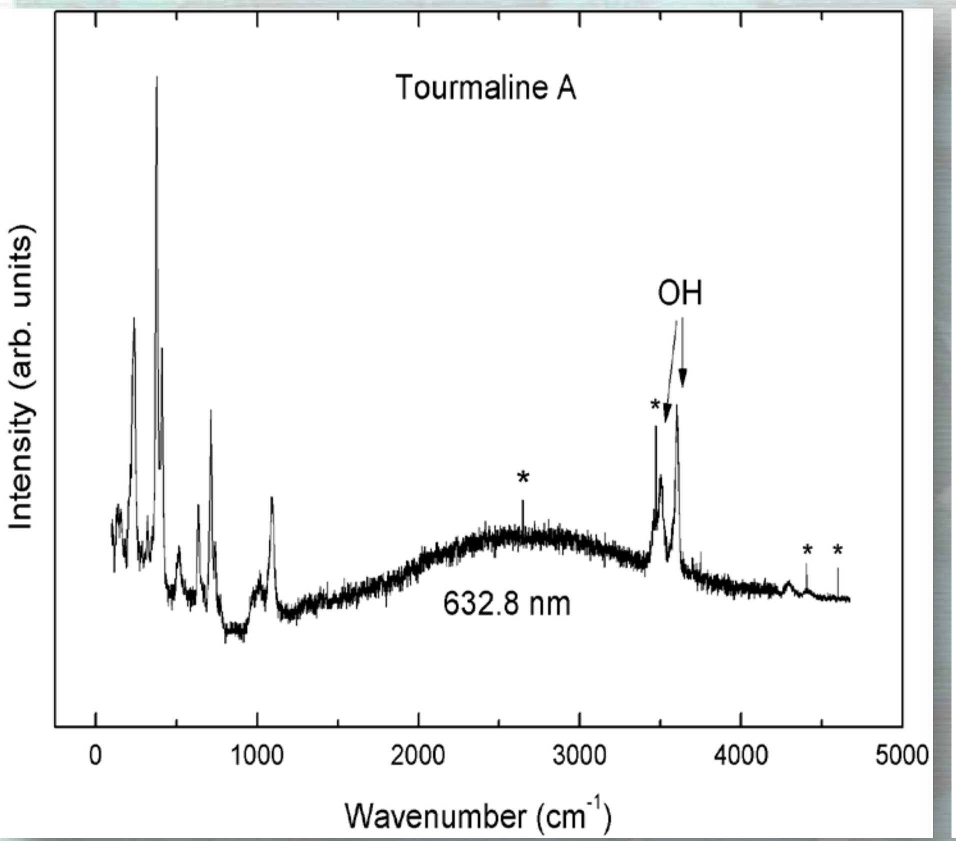
N, Si, V defects in diamonds

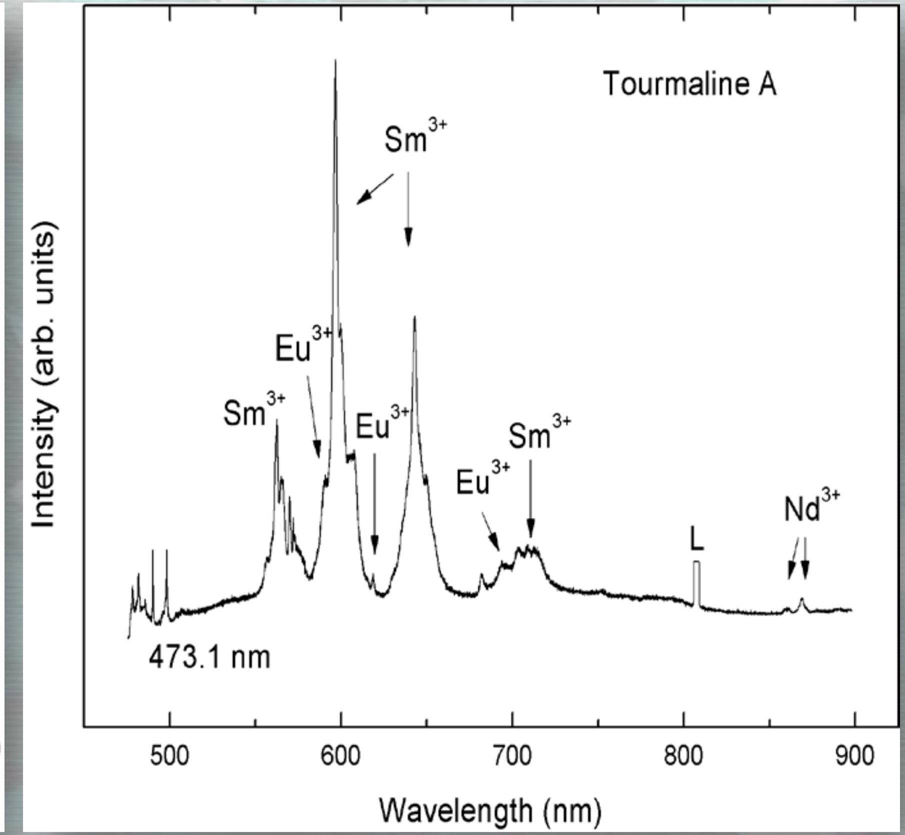
C. M. Breeding , W. Wang, Diamond & Related Materials 17 (2008) 1335–1344



REE PL in Tourmaline (liddicoatite)

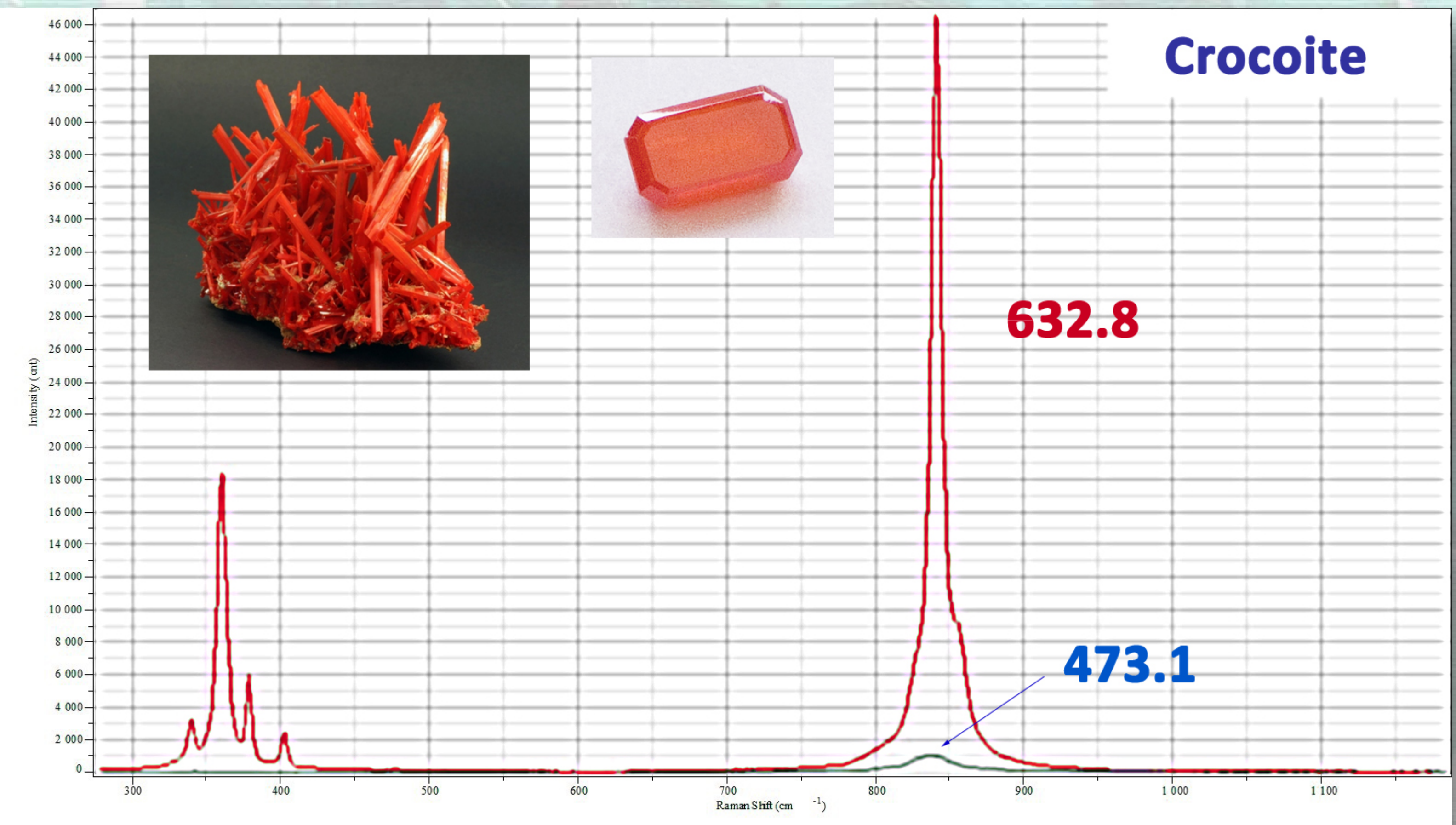




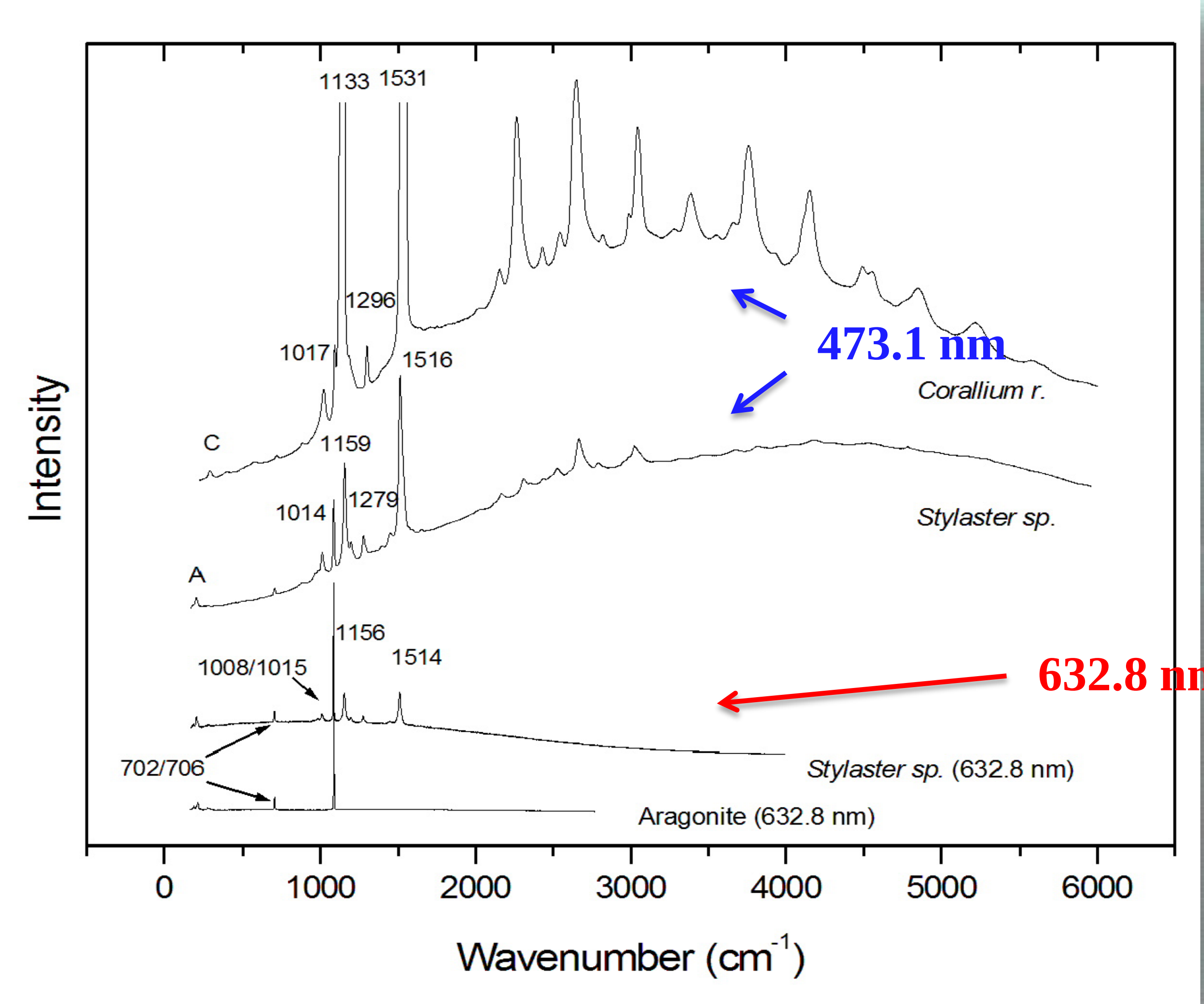


RESONANCE

Crocoite resonance



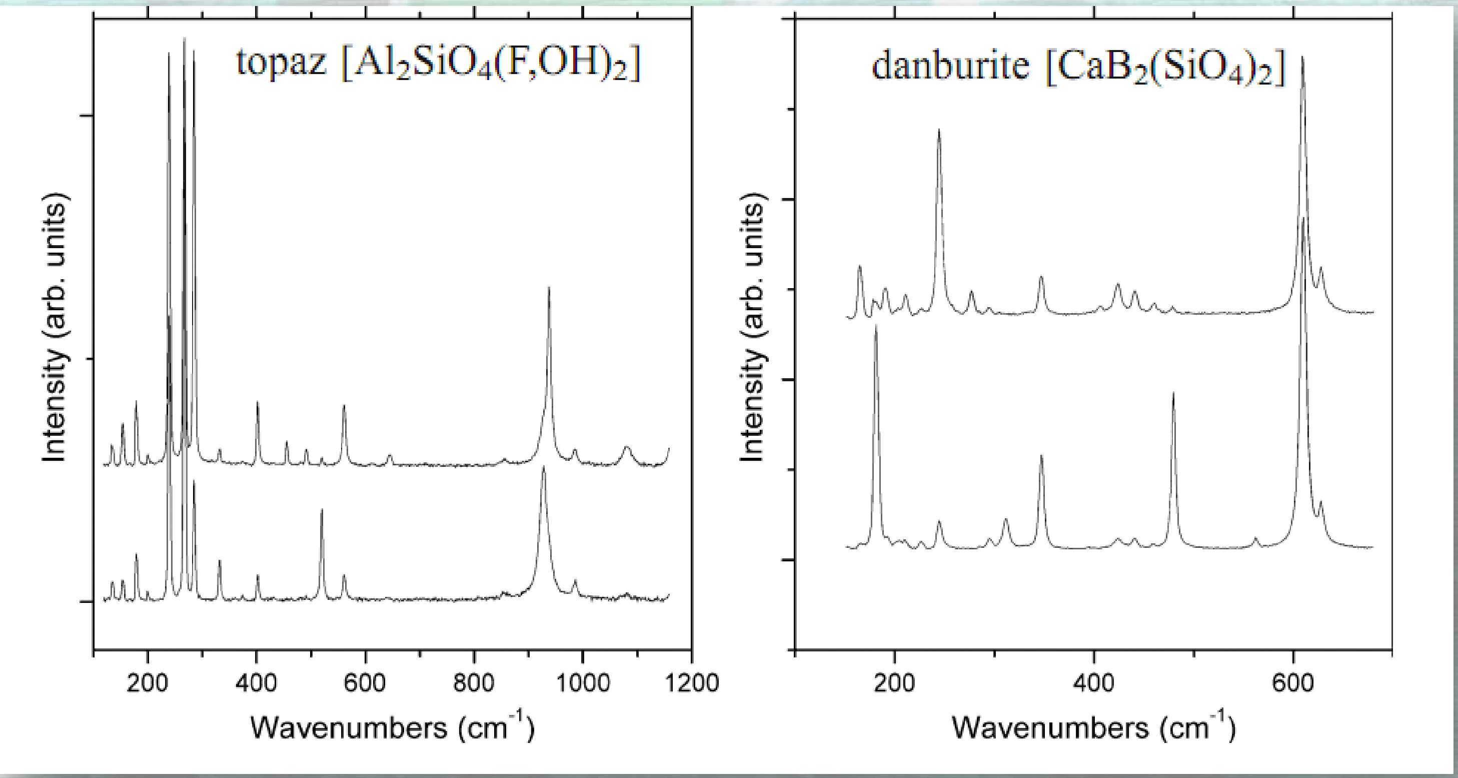
Carotenoid resonance in corals



473.1 nm

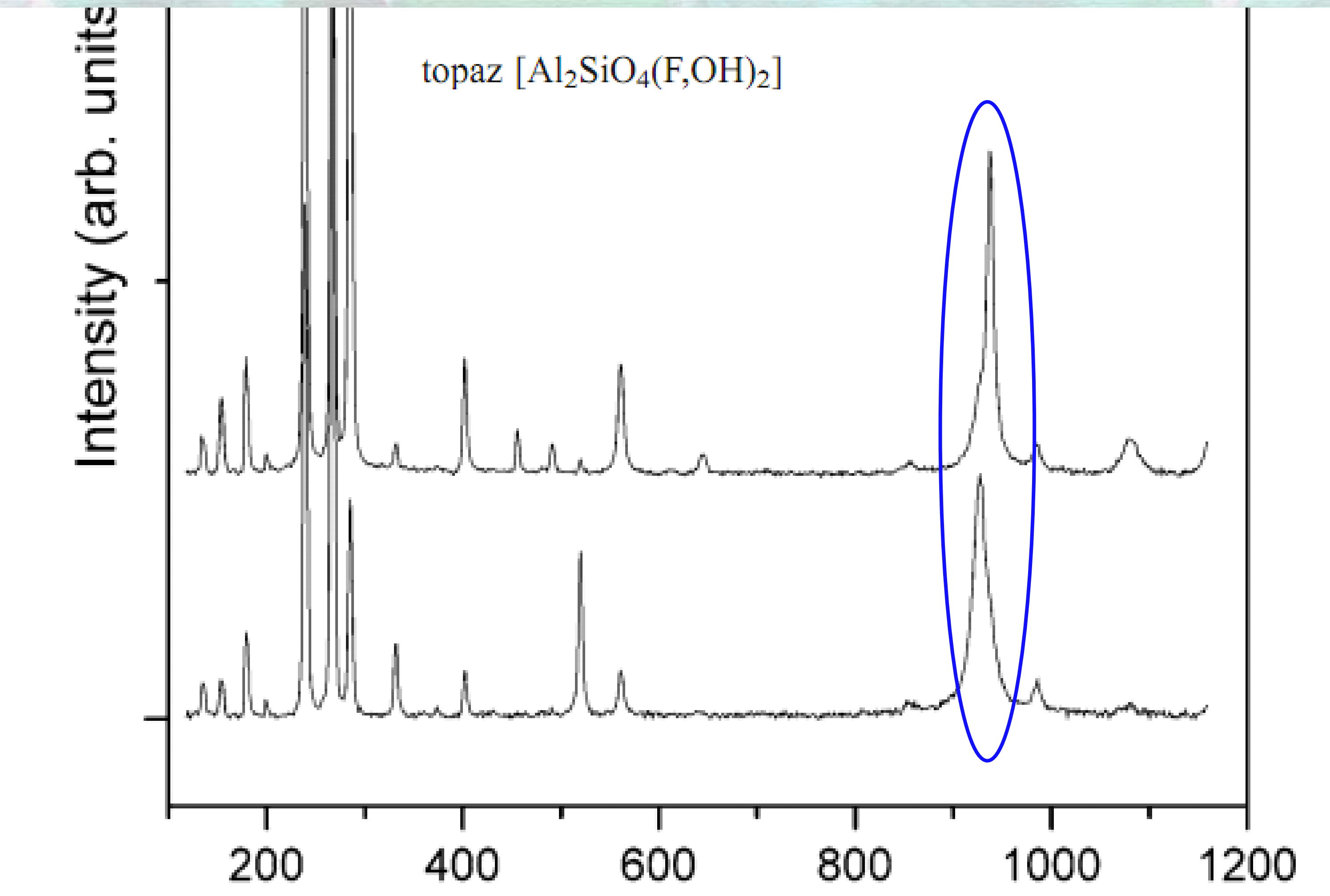
632.8 nm

Orientation



- **Relative peak intensity depends on the mutual orientation of light polarization and crystal axis.**
- **Possible information on symmetry and geminations.**
- **Problem for databases**

Orientation



Warning: fake shift!

2) COMPOSITION

Composition : nephritic jades

nephrite

$(Ca_2(Mg^{2+},Fe^{2+})_5Si_8O_{22}(OH)_2)$

Series *tremolite (Mg-rich term)*

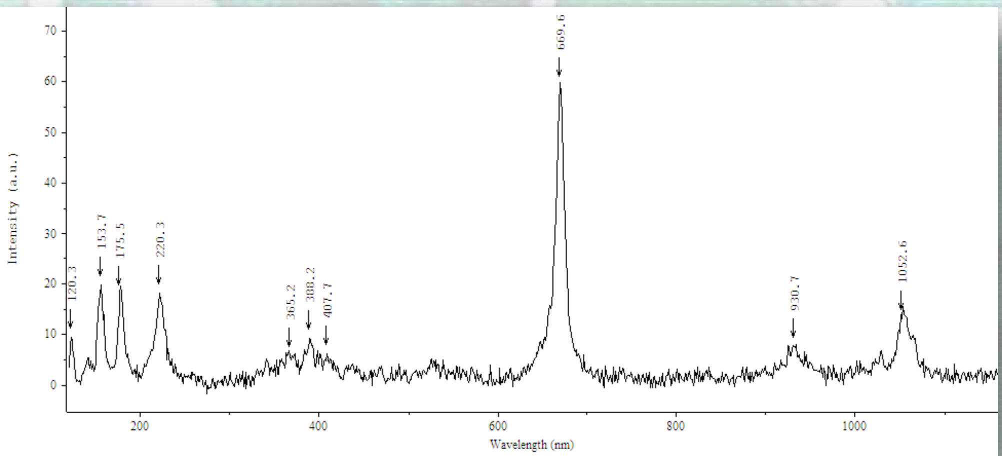
- ferroactinolite (Fe-rich term)

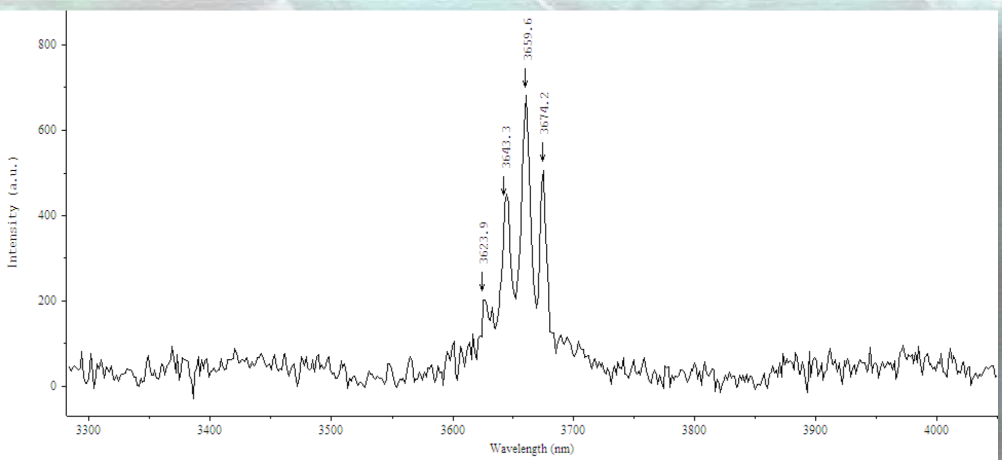
$X=Mg/(Mg^{+}+Fe^{2+})$

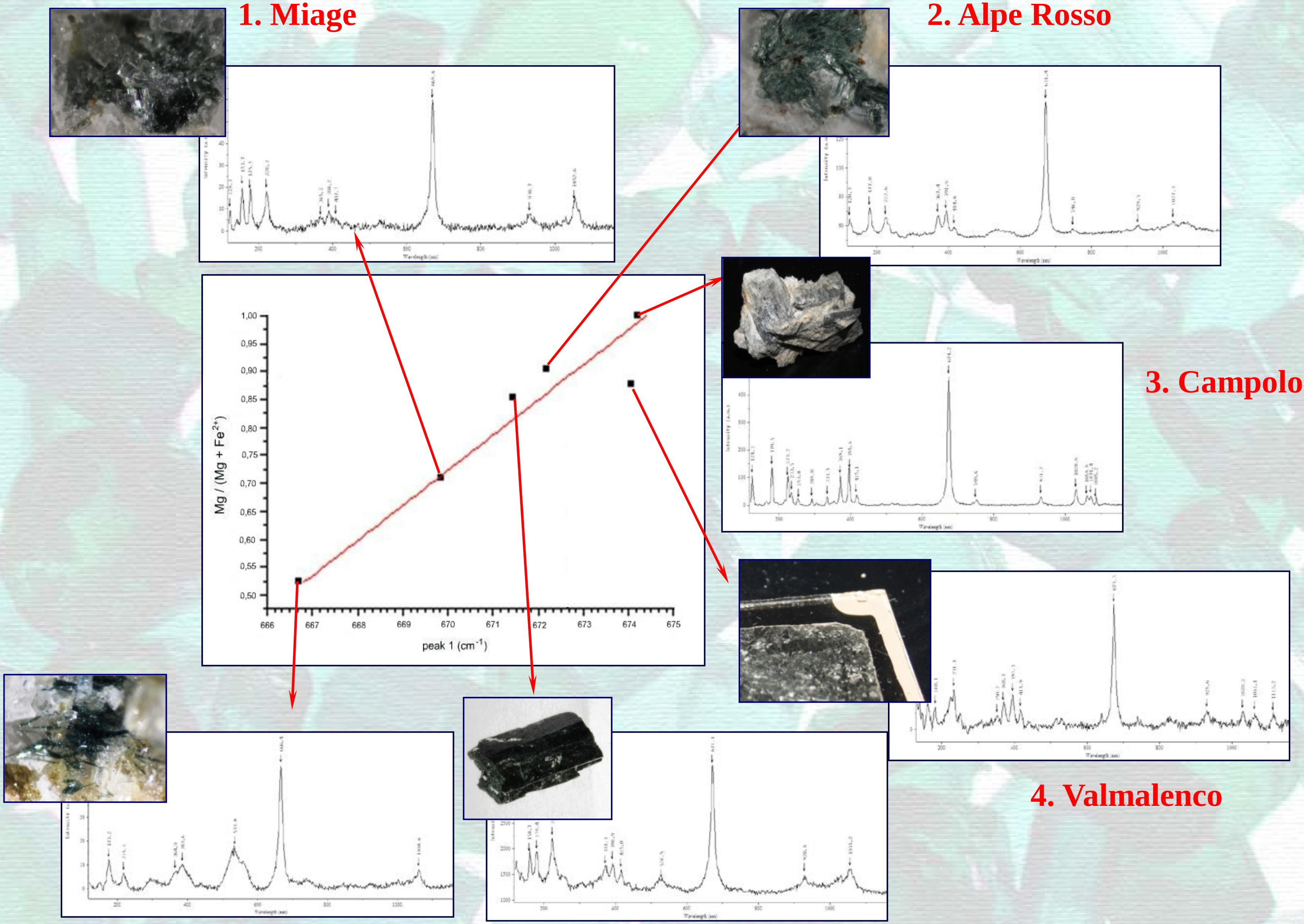
$X \geq 0.9$ tremolite

$0.5<X<0.9$ actinolite

$X<0.5$ ferro-actinolite







1. Miage

2. Alpe Rosso

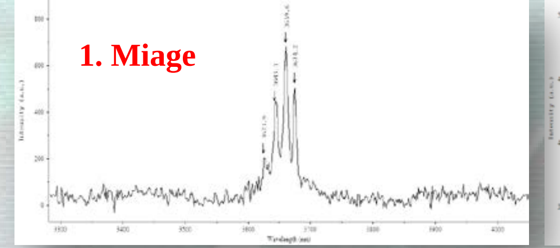
3. Campolongo

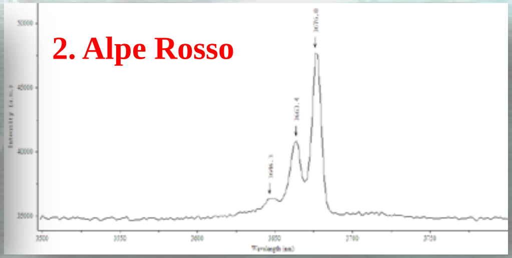
4. Valmalenco

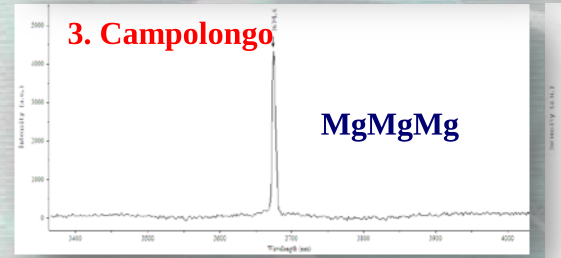
5. Pizzo Bandiera

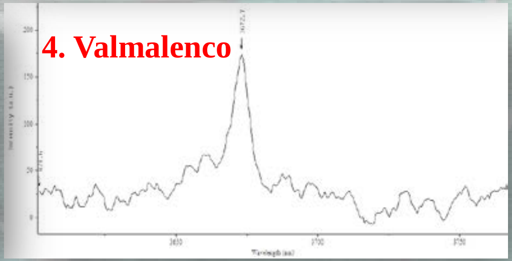
6. Pizzo Rosso

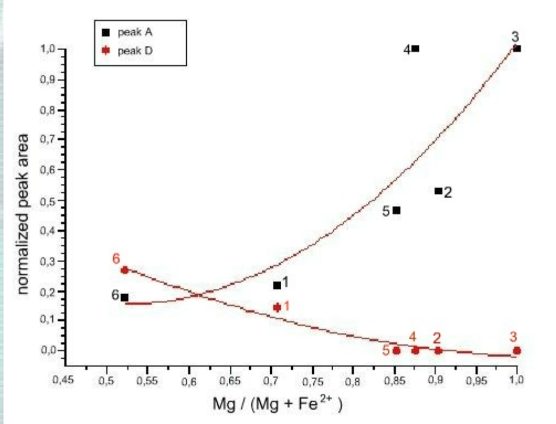
OH stretching region in nephrites











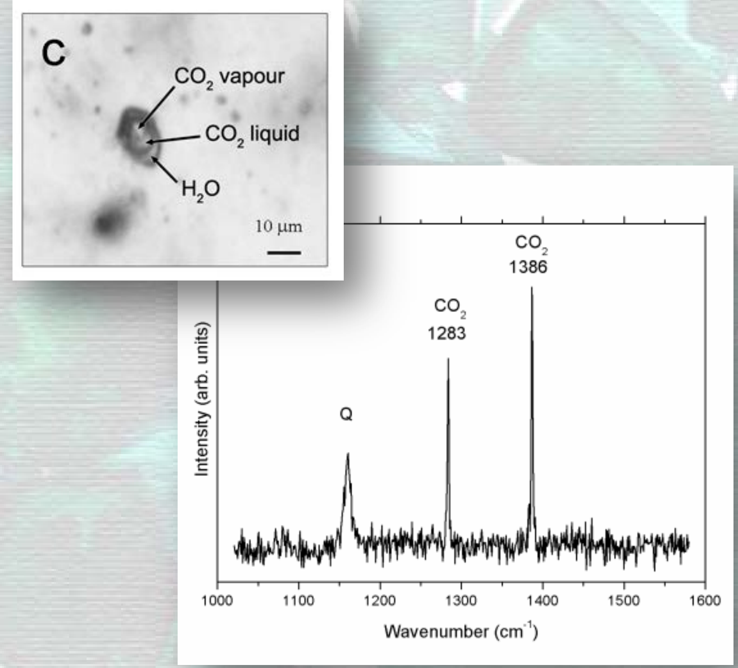
Different Mg, Fe occupancies around the OH site

3) NATURE - GENESIS

Fluid inclusions

Inclusions in Quartz

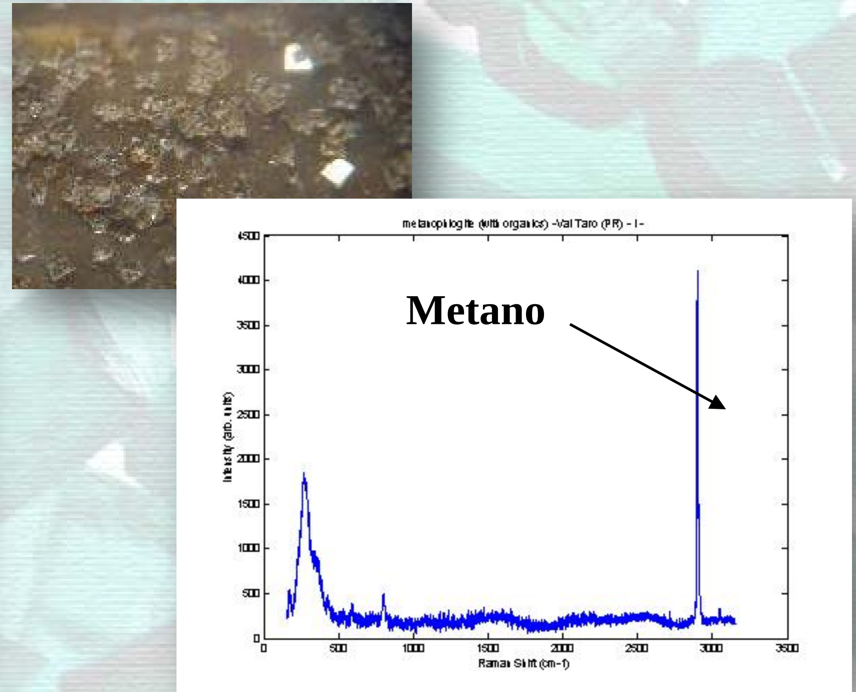
(Honduras)



D. Bersani, E. Salvioli-Mariani, M. Mattioli, M. Menichetti, P.P. Lottici, ,Spectrochim. Acta A

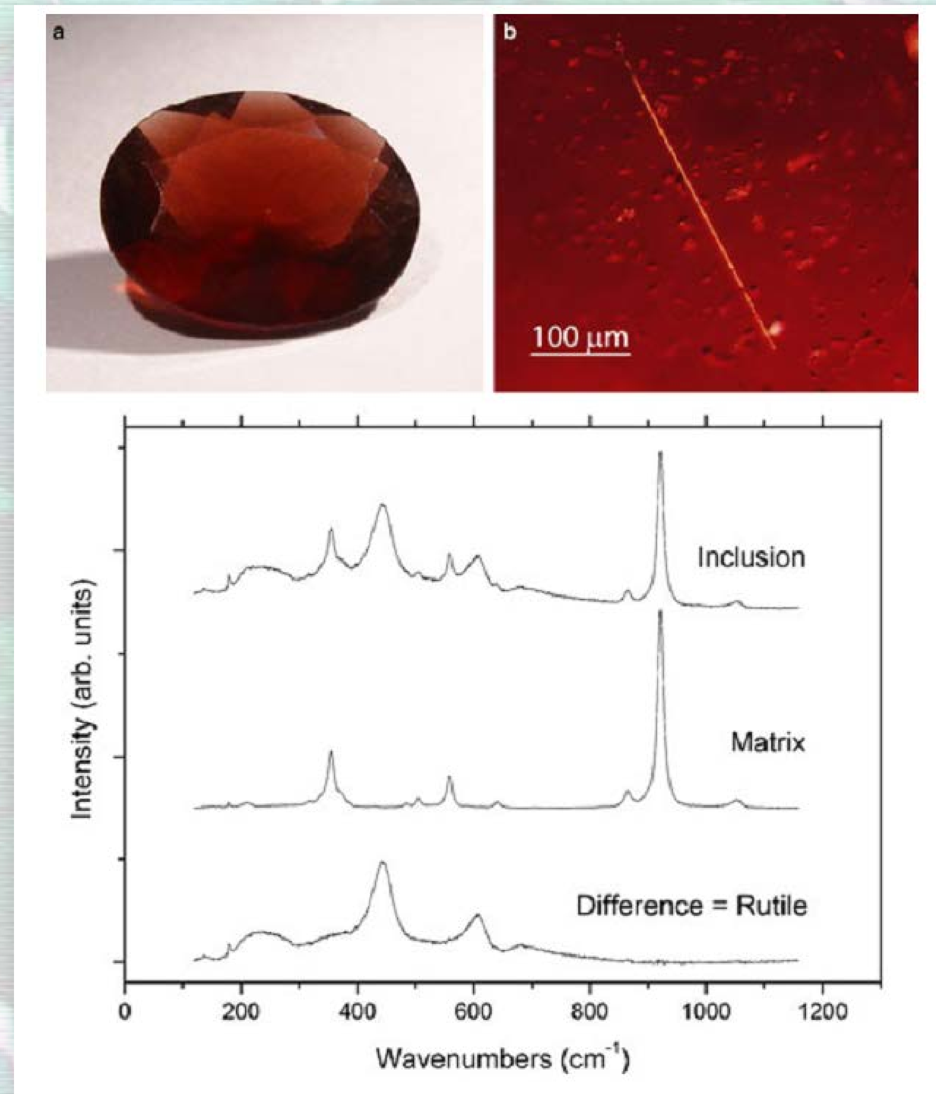
Melanophlogite

(Parma - Italy)



M.Tribaudino, A. Artoni, C. Mavris, D. Bersani, P. P. Lottici, D. Belletti, Amer. Mineralogist 93, 88–94 (2008)

Solid inclusions



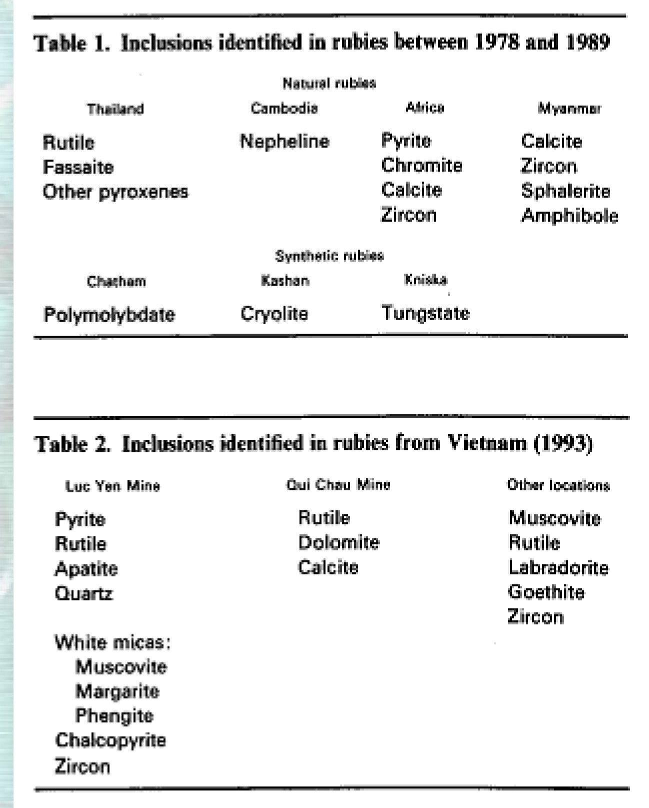


Table 1. Inclusions identified in rubies between 1978 and 1989

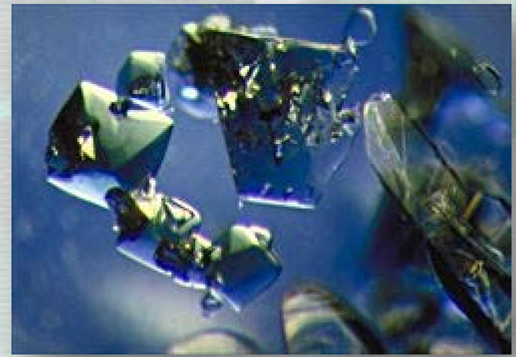
Natural rubies			
Thailand	Cambodia	Africa	Myanmar
Rutile Fassaite Other pyroxenes	Nepheline	Pyrite Chromite Calcite Zircon	Calcite Zircon Sphalerite Amphibole

Synthetic rubies		
Chatham	Kashan	Kniska
Polymolybdate	Cryolite	Tungstate

Table 2. Inclusions identified in rubies from Vietnam (1993)

Luc Yen Mine	Qui Chau Mine	Other locations
Pyrite Rutile Apatite Quartz White micas: Muscovite Margarite Phengite Chalcopyrite Zircon	Rutile Dolomite Calcite	Muscovite Rutile Labradorite Goethite Zircon

M. L. Dele et al. J. Raman Spectr. 28 (1997)



Rutile in ruby

Magmatic vs. metamorphic sapphires inclusions

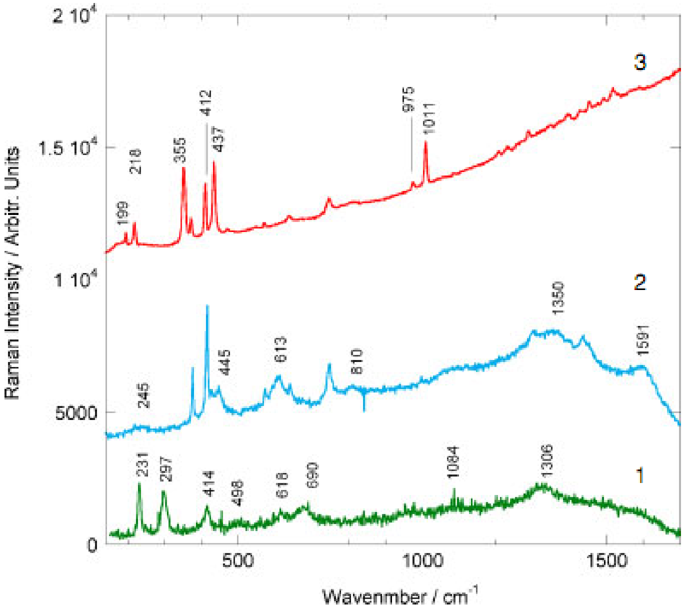


Figure 4. Raman spectra at room temperature of inclusions in magmatic sapphires: 1, hematite from Australia; 2, rutile and graphite from Tanzania; 3, zircon from alkali basalts.

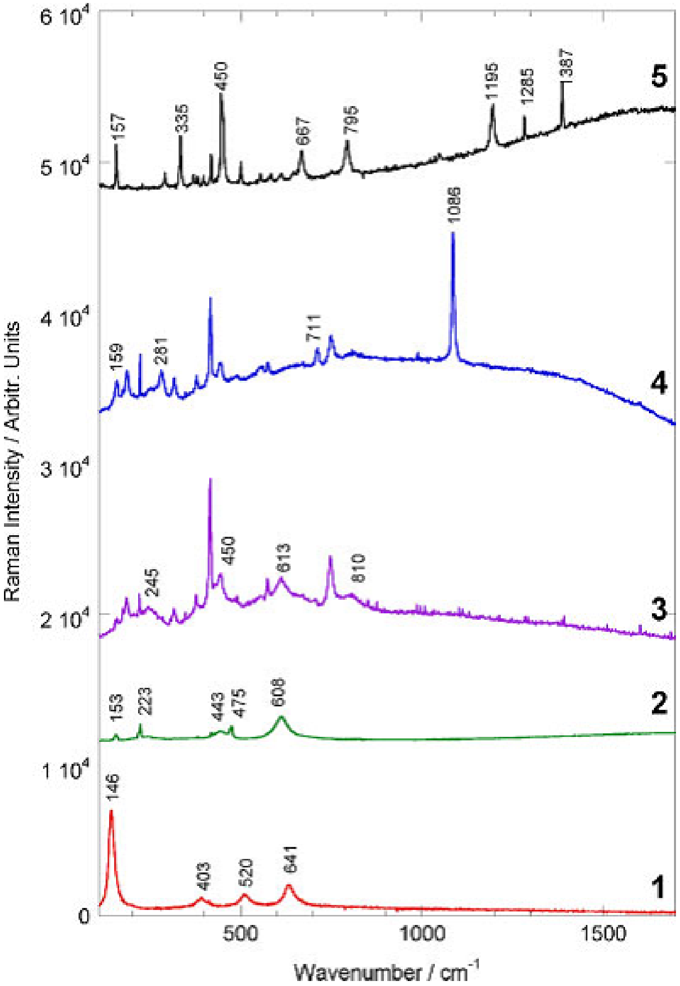
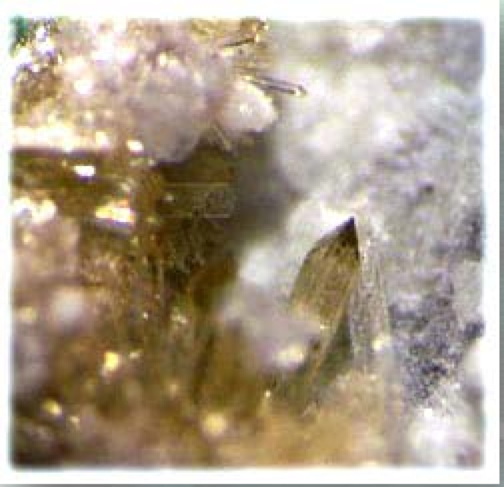


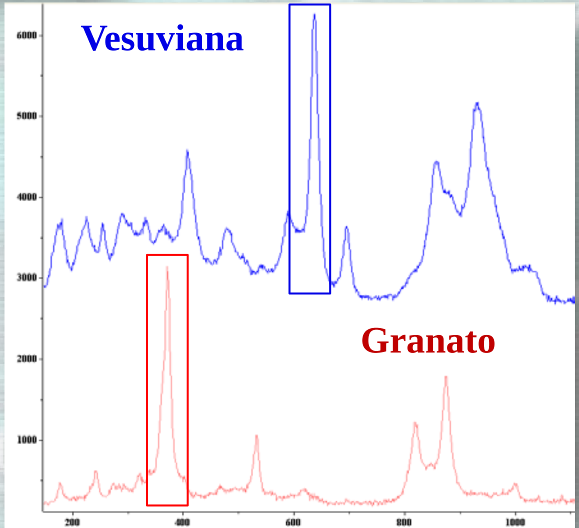
Figure 3. Raman spectra at room temperature of inclusions in metamorphic sapphires: 1, anatase from Vietnam; 2, rutile and sulfur from Sri Lanka; 3, rutile from Madagascar; 4, calcite from Madagascar; 5, diaspore and CO_2 from Sri Lanka.

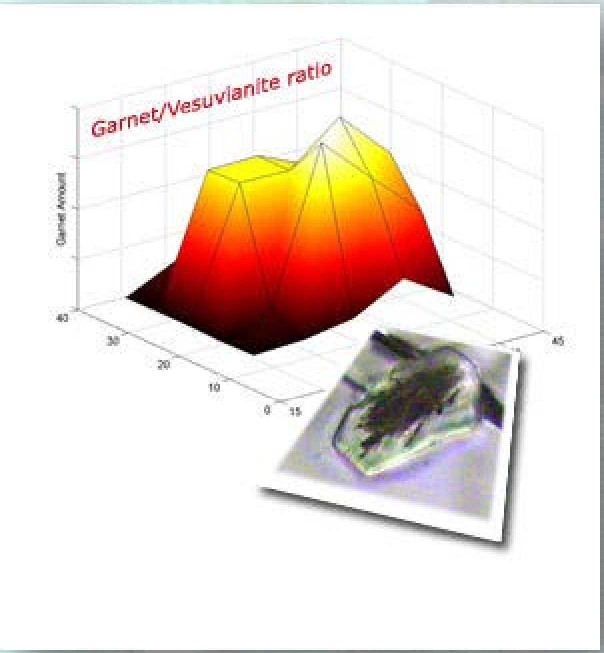
V. Palanza et al., J. Raman Spectrosc. 2008; 39: 1007–1011

Spectral maps



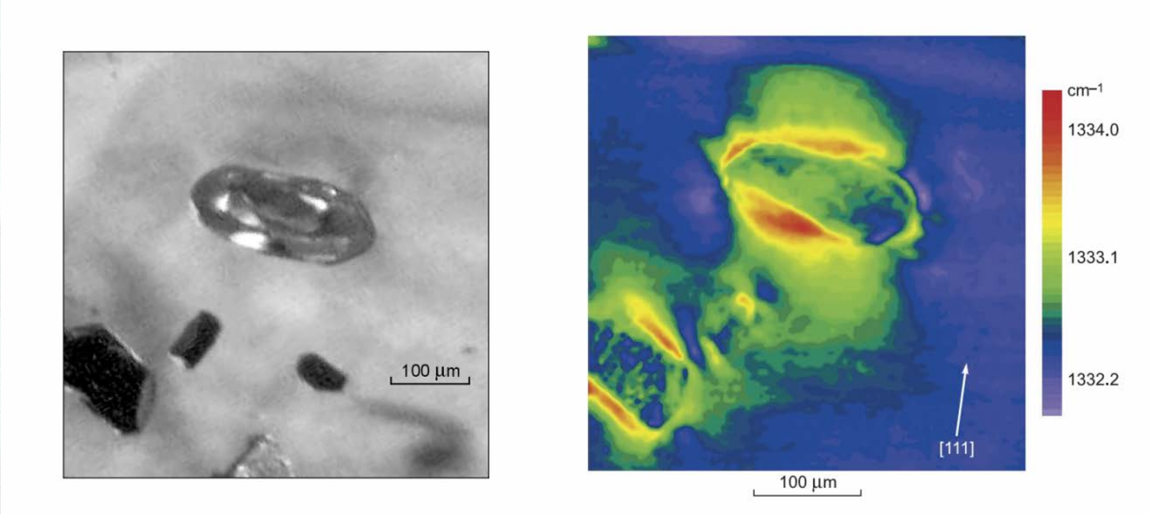
Matrix of spectra

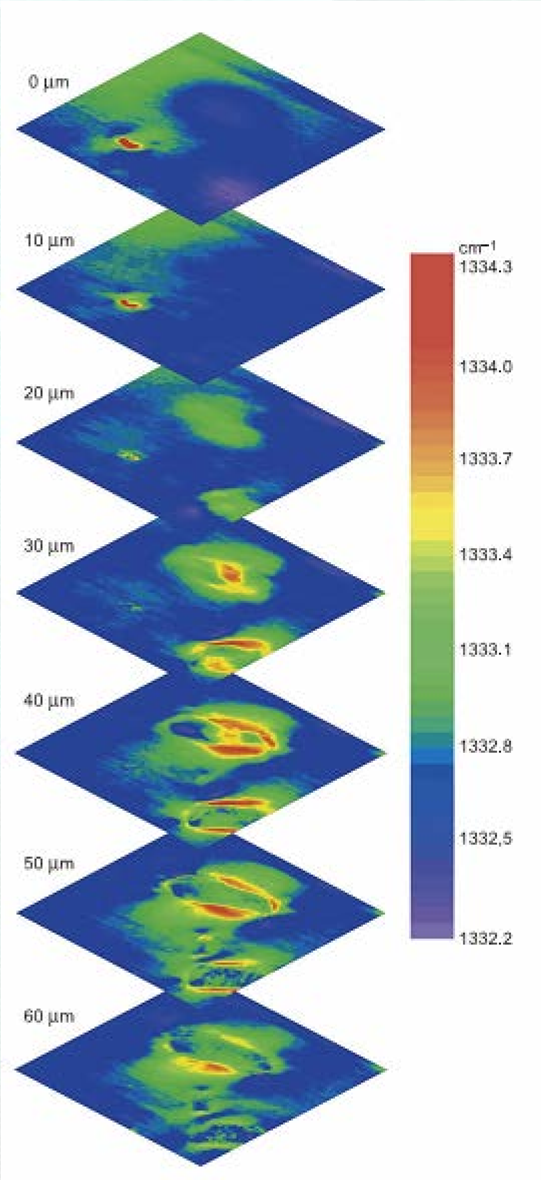




Intensity ratio map

Determination of the genesis conditions of diamonds: residual pressure around the inclusions

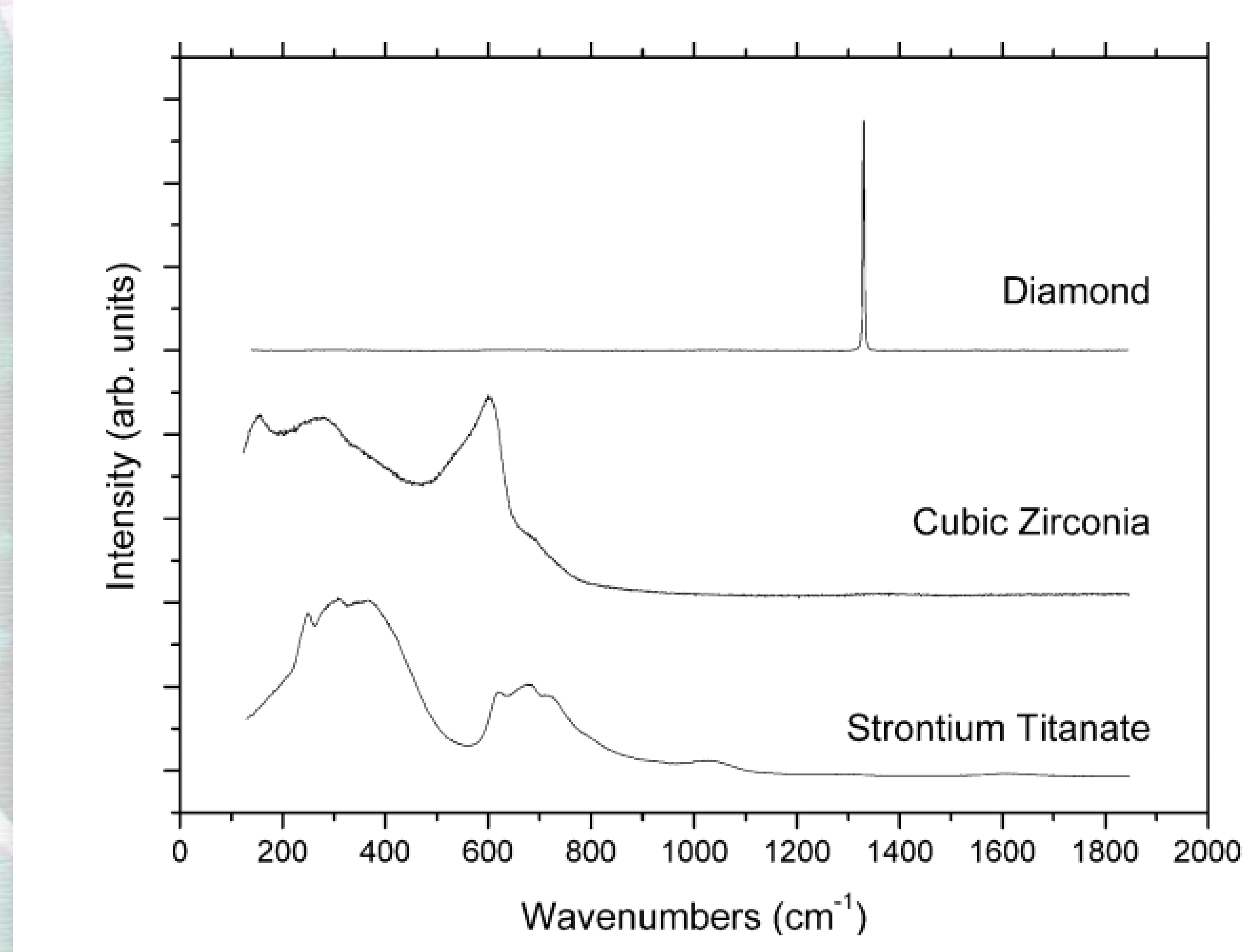




- **Chromite and Olivine inclusions: 3D Raman map of the position of the 1332 cm^{-1} diamond peak (shift proportional to P)**
- **The elastic properties of the matrix are realted to the formation depth**

H. Kagi et al. / Russian Geology and Geophysics 50 (2009) 1183–1187

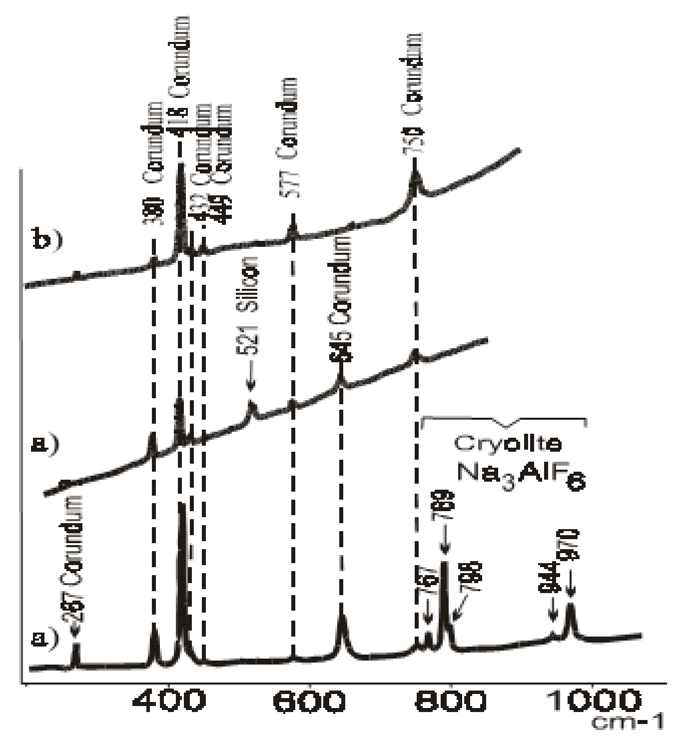
Simulants



Intensity (arb. units)
Diamond
Cubic Zirconia
Strontium Titanate
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Wavenumbers (cm^{-1})

Synthetics: solid and fluid inclusions

Verneuil synthesis	Inclusions described in literature	Raman microspectroscopy (Jobin - Yvon T-64000 laser Ar =514.5 nm)
Experimental laboratory of the former Huta Aluminium in Skawina	Gas bubbles Platinum Cryolite	Cryolite Silicon
R. Fremy (1903)	No date	Not found

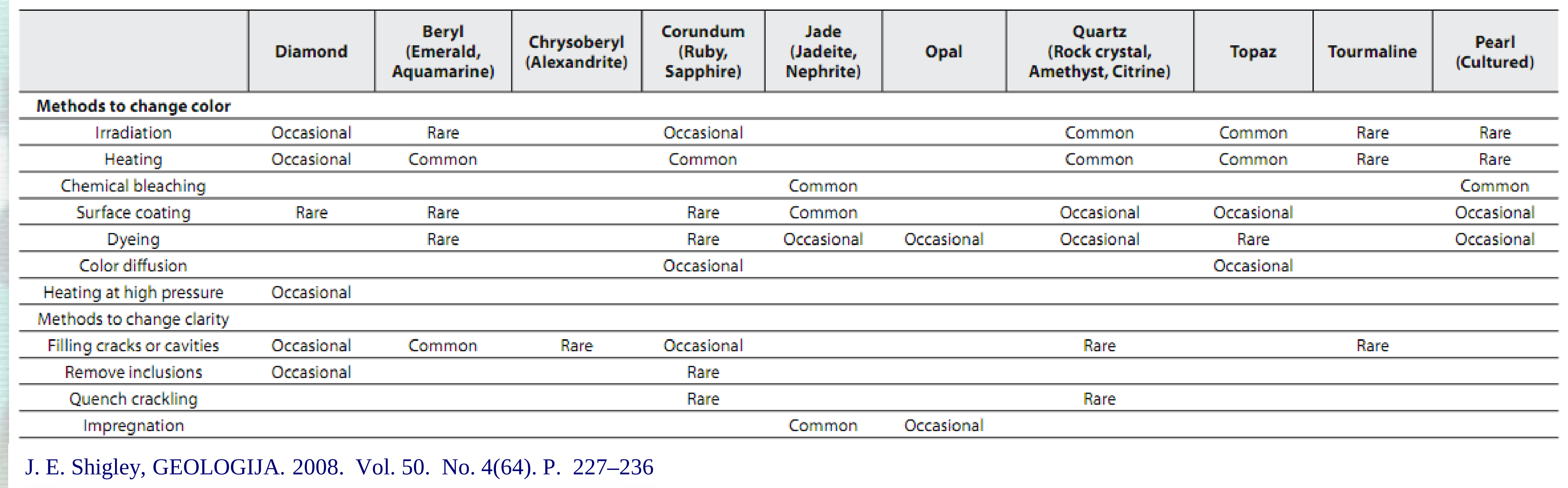


Cryolite in synthetic rubies

Delé ML et al. (1997) J Raman Spectrosc 28:673–676

4) TREATMENTS

Some enhancement treatments

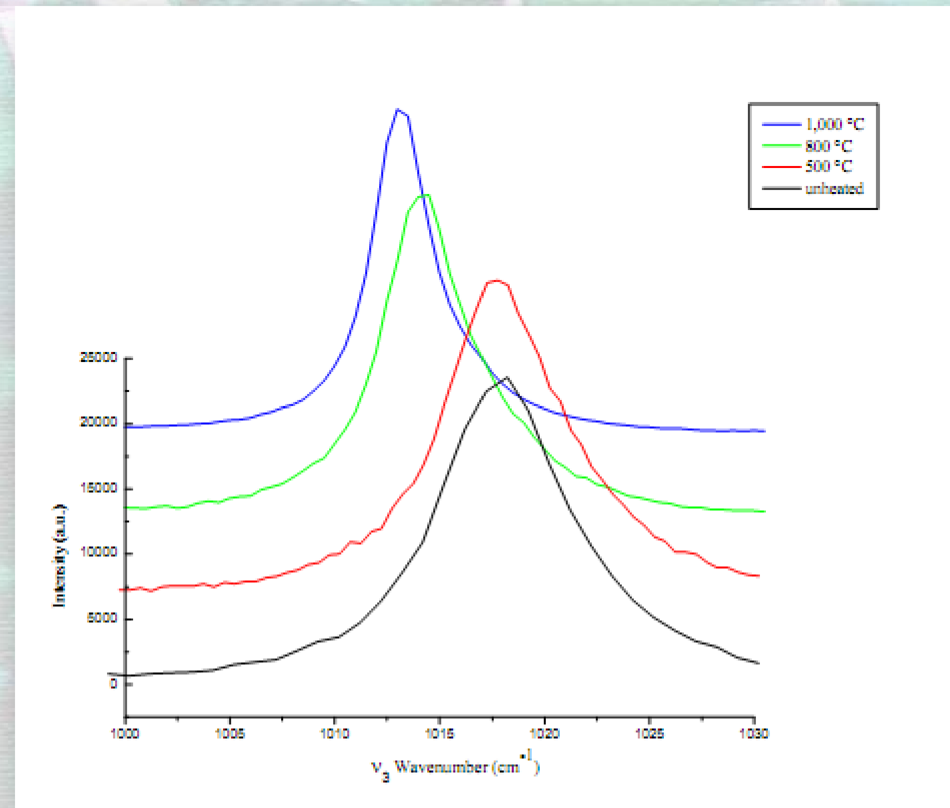


	Diamond	Beryl (Emerald, Aquamarine)	Chrysoberyl (Alexandrite)	Corundum (Ruby, Sapphire)	Jade (Jadeite, Nephrite)	Opal	Quartz (Rock crystal, Amethyst, Citrine)	Topaz	Tourmaline	Pearl (Cultured)
Methods to change color										
Irradiation	Occasional	Rare		Occasional			Common	Common	Rare	Rare
Heating	Occasional	Common		Common			Common	Common	Rare	Rare
Chemical bleaching					Common					Common
Surface coating	Rare	Rare		Rare	Common		Occasional	Occasional		Occasional
Dyeing		Rare		Rare	Occasional	Occasional	Occasional	Rare		Occasional
Color diffusion				Occasional				Occasional		
Heating at high pressure	Occasional									
Methods to change clarity										
Filling cracks or cavities	Occasional	Common	Rare	Occasional			Rare		Rare	
Remove inclusions	Occasional			Rare						
Quench crackling				Rare			Rare			
Impregnation					Common	Occasional				

J. E. Shigley, GEOLOGIJA. 2008. Vol. 50. No. 4(64). P. 227–236

It’s important to discriminate between “allowed” and “not-allowed” treatments.

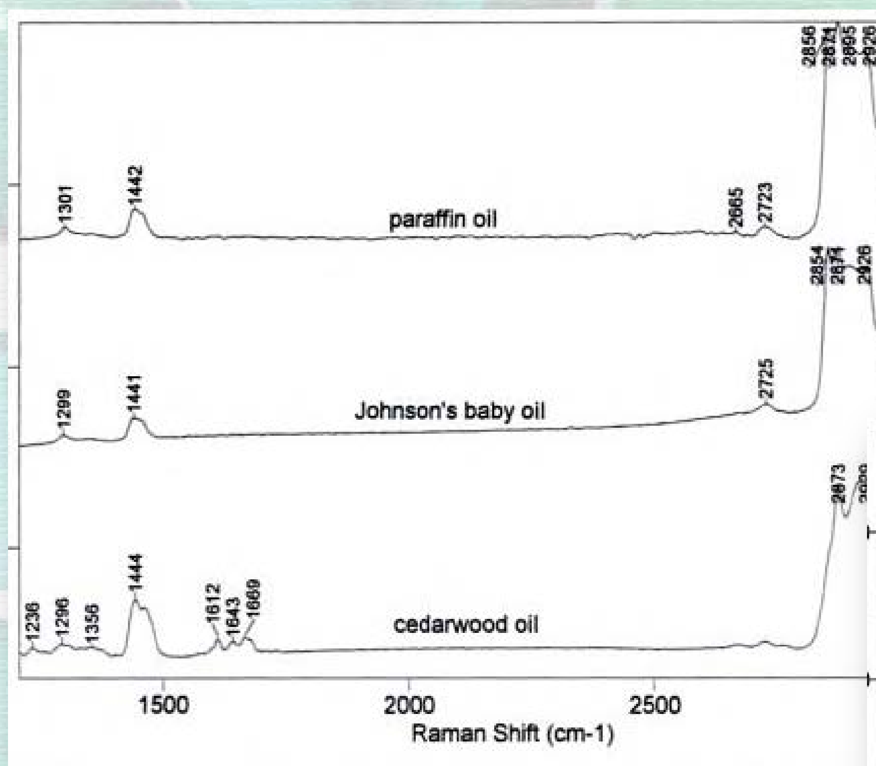
Bandwidth as order indicator (genesis, treatments, metamictization)

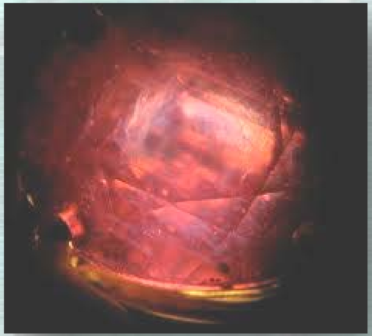


Sharpening and red-shift of a zircon peak after annealing

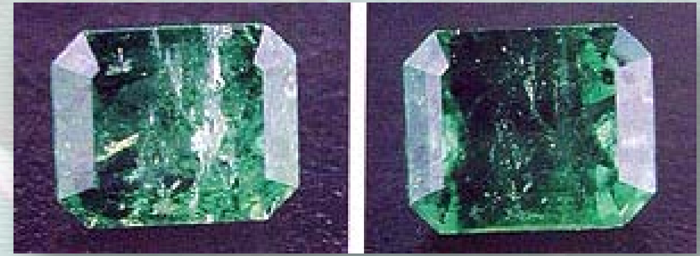
Thesys c/o univ. Mainz - Bhuwadol Wanthanachaisaeng

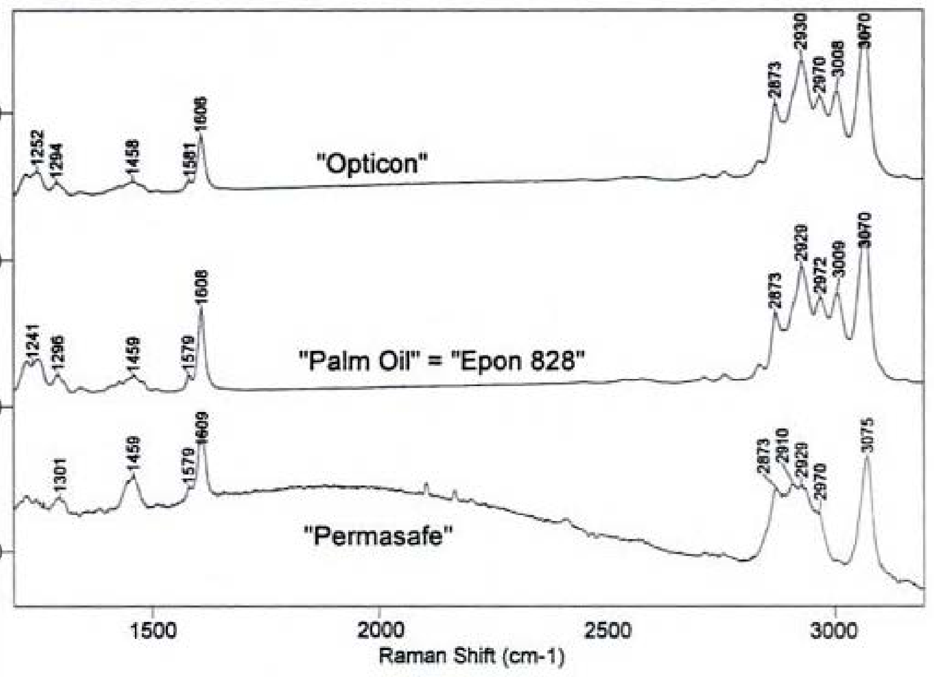
“Allowed” fillers





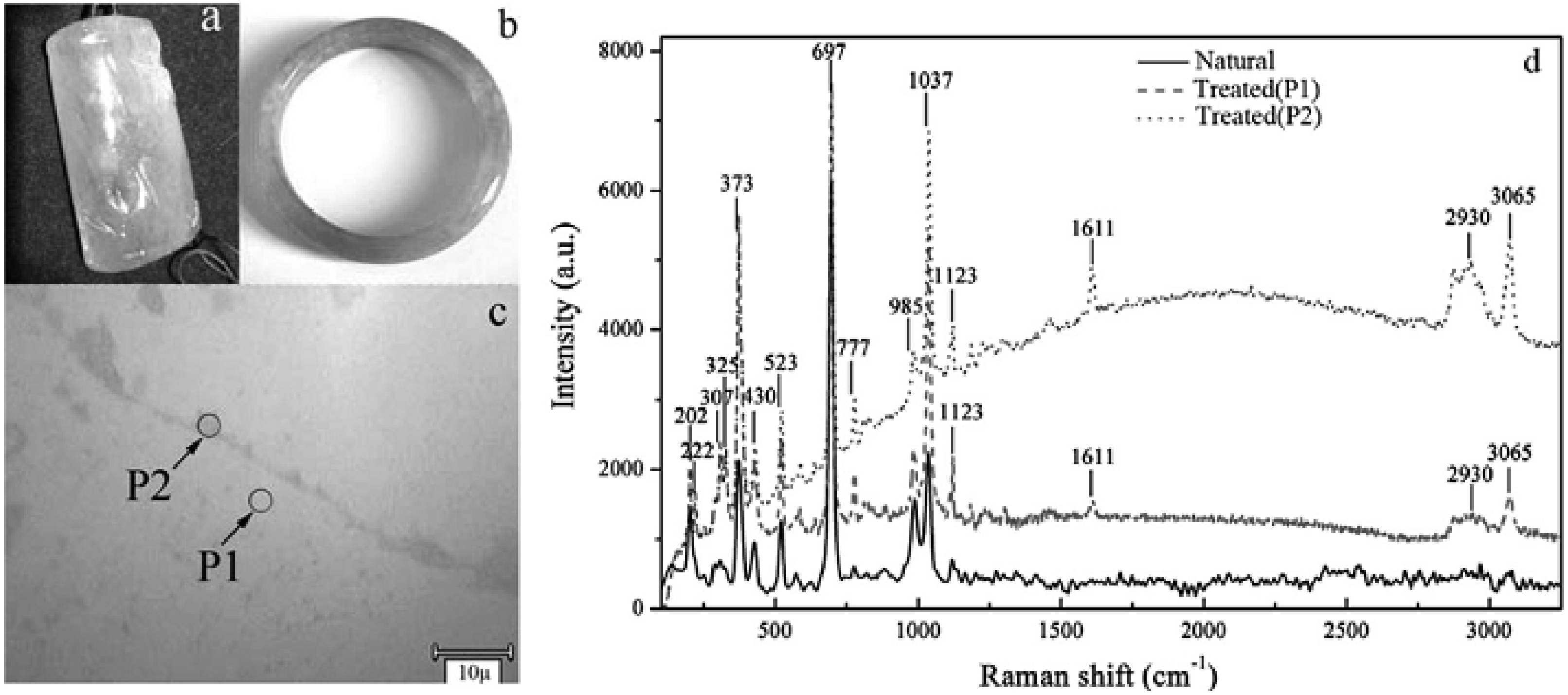
“Non allowed” fillers





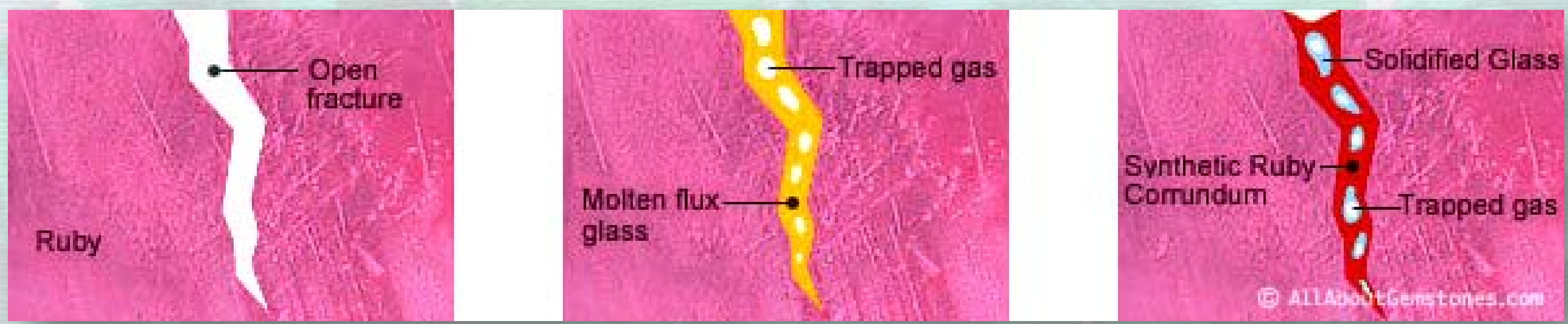
Kiefert L, Hanni HA, Ostertag T (2001) In: Lewis IR, Edwards HGM (eds) Handbook of Raman spectroscopy: from the research laboratory to the process line. Marcel Dekker, New York, pp 469–490;

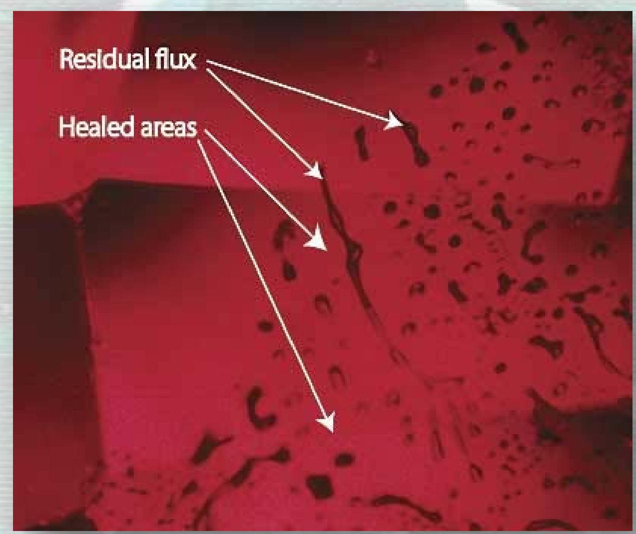
Jadeite “fissure filling” with epoxy resin



Jian-Liang Fan et al., Spectroscopy Letters, 42:129–135, 2009

“Flux Healing”

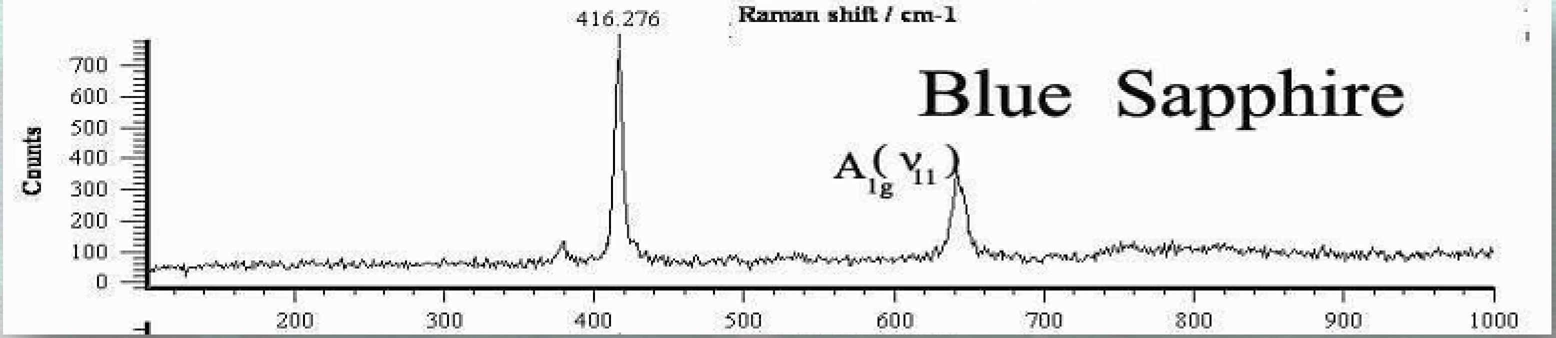


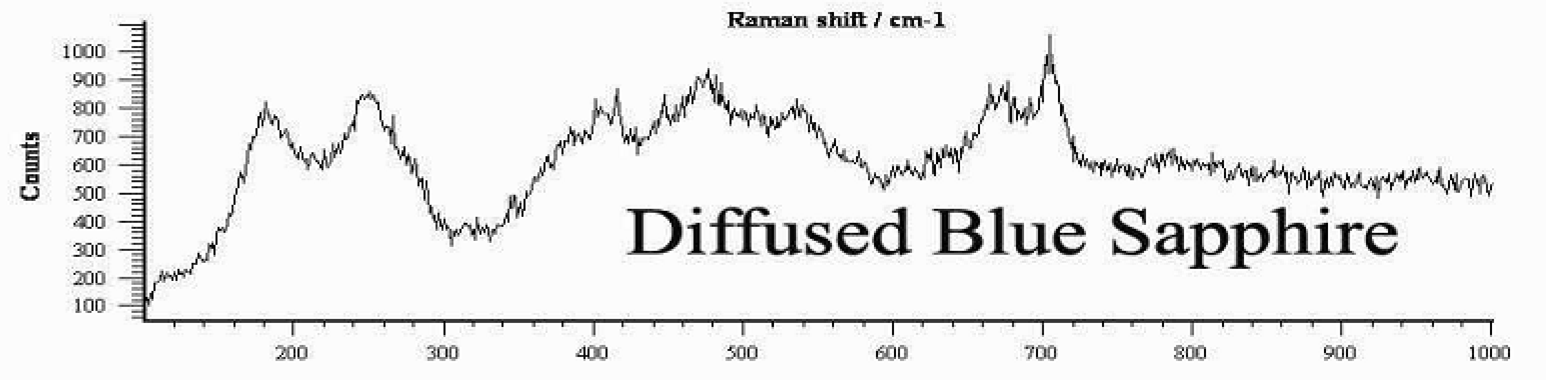


Hi-T treatment with flux: some flux residuals can be detected by Raman.

http://www.allaboutgemstones.com/gemstones_ruby_enhancements.html
and del Castillo HC et al., (2009) Anal Bioanal. Chem 394:1043–1058

Saffire enhancement: beryllium diffusion by hi-T solid-state reaction with chrysoberyl

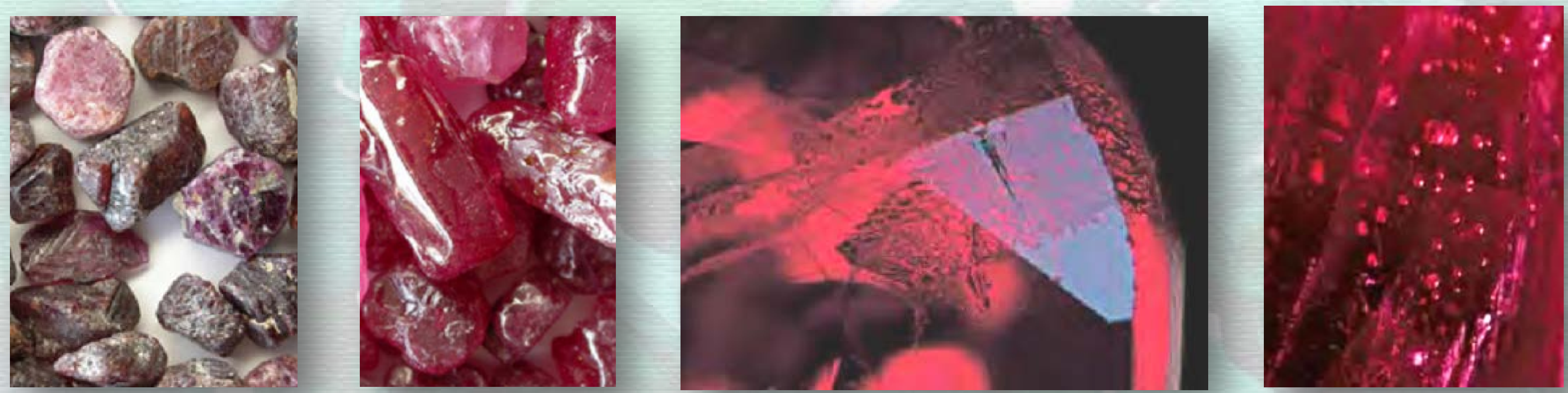


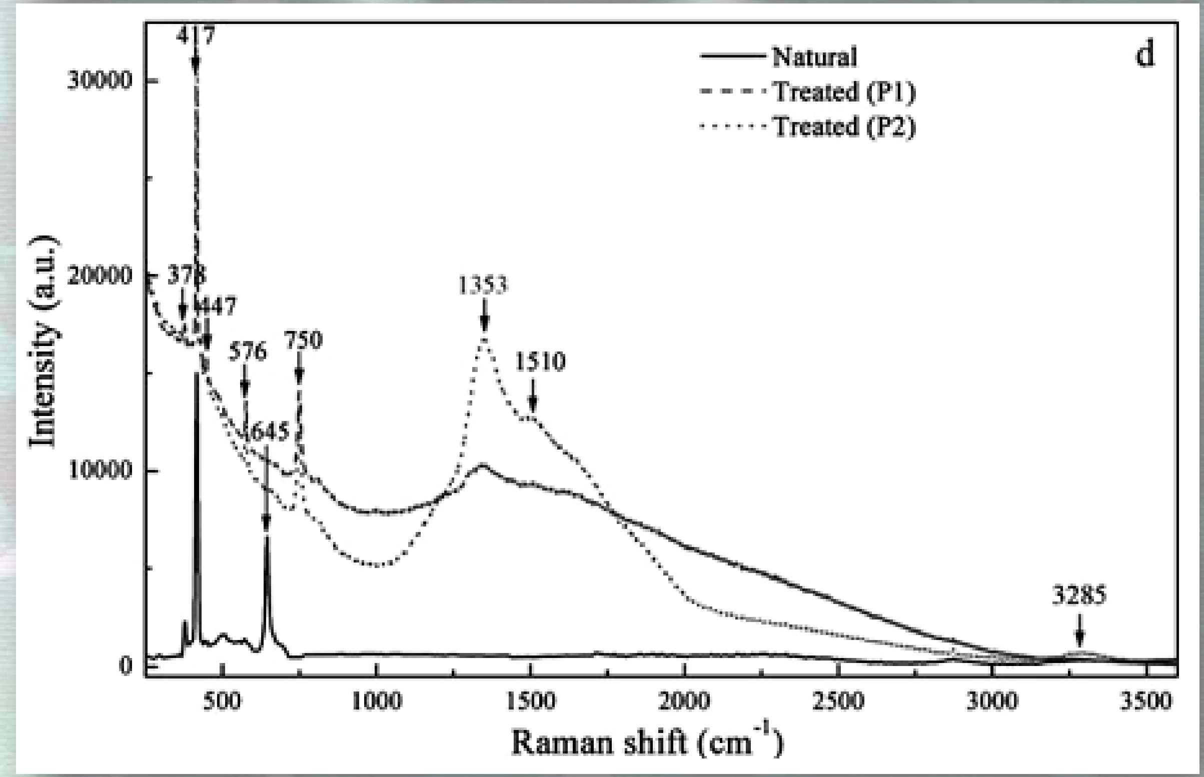


Partial amorphization shown by the Raman spectrum

M.D. Sastry et al., IOP Conf. Series: Materials Science and Engineering 2 (2009) 012007

Hard to identify treatment: lead glass filling





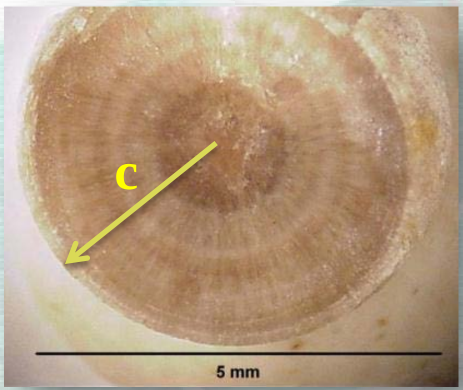
Broad band between 1300 and 1600 cm^{-1} [Fan et al]

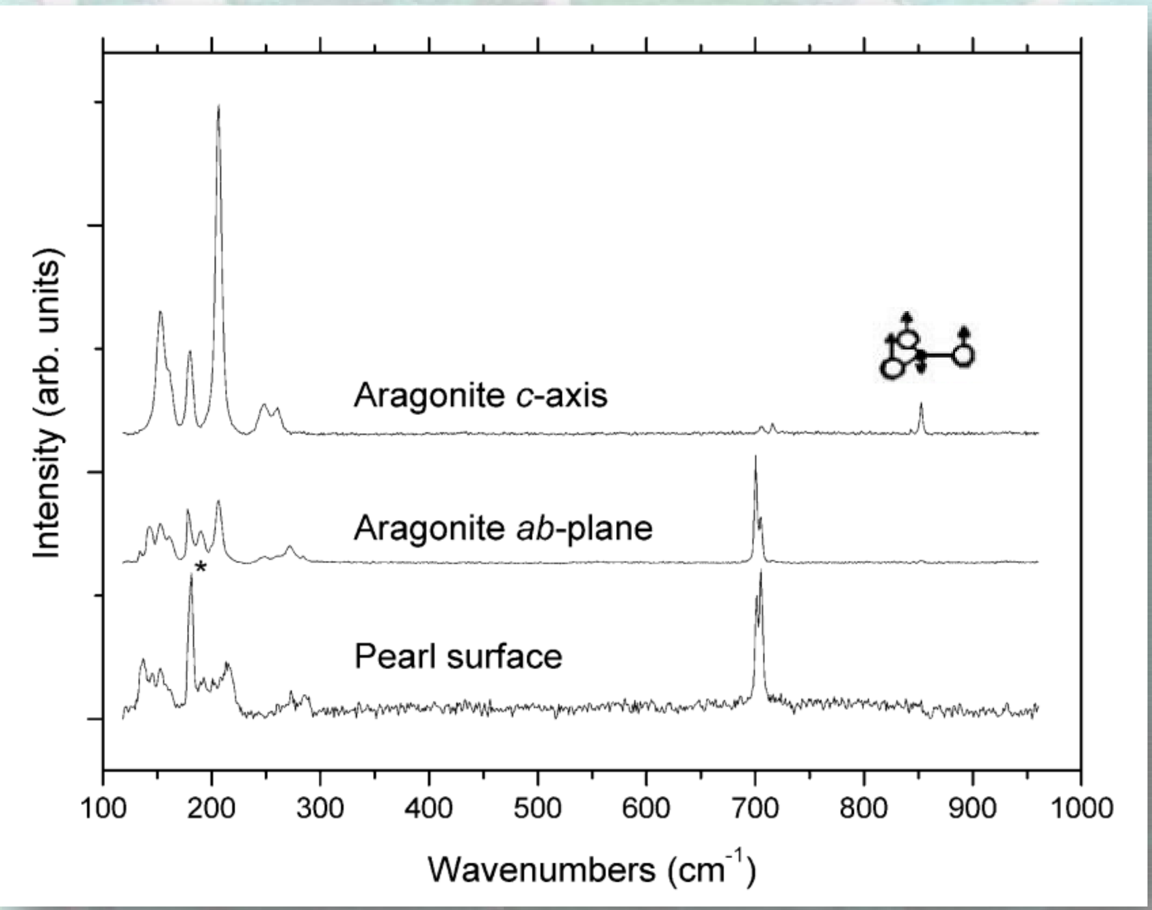
Shane F. McClure, Christopher P. Smith, Wuyi Wang, and Matthew Hall GEMS & GEMOLOGY, Vol. 42, No. 1, pp. 22–34.

Fan J-L, Guo S-G, Liu X-L (2009) Spectrosc Lett 42:129–135

5) ORGANIC - ORGANOGENIC

Organic gems: pearls



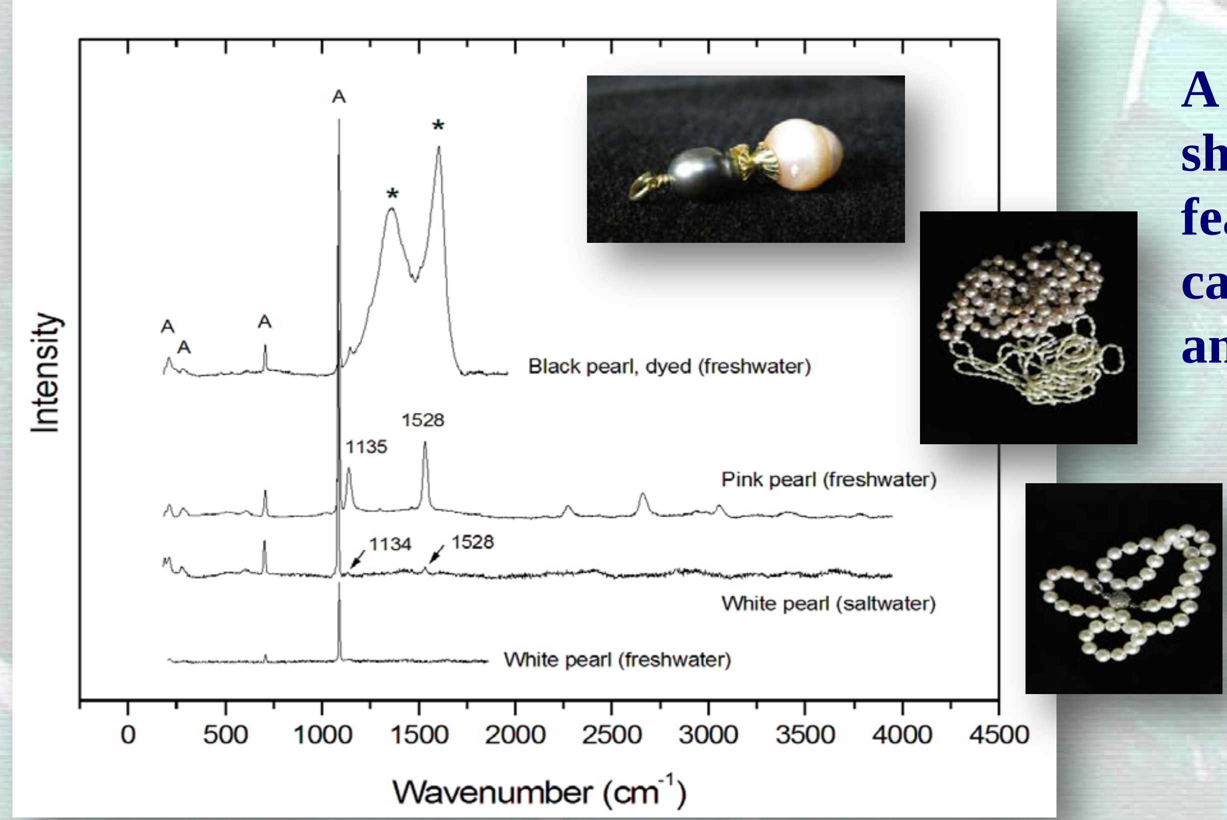


The out-of-plane bending (856 cm^{-1}) is visible in aragonite only in polarization parallel to *c*-axis.

But on the pearls surface only the *ab* plane emerges.

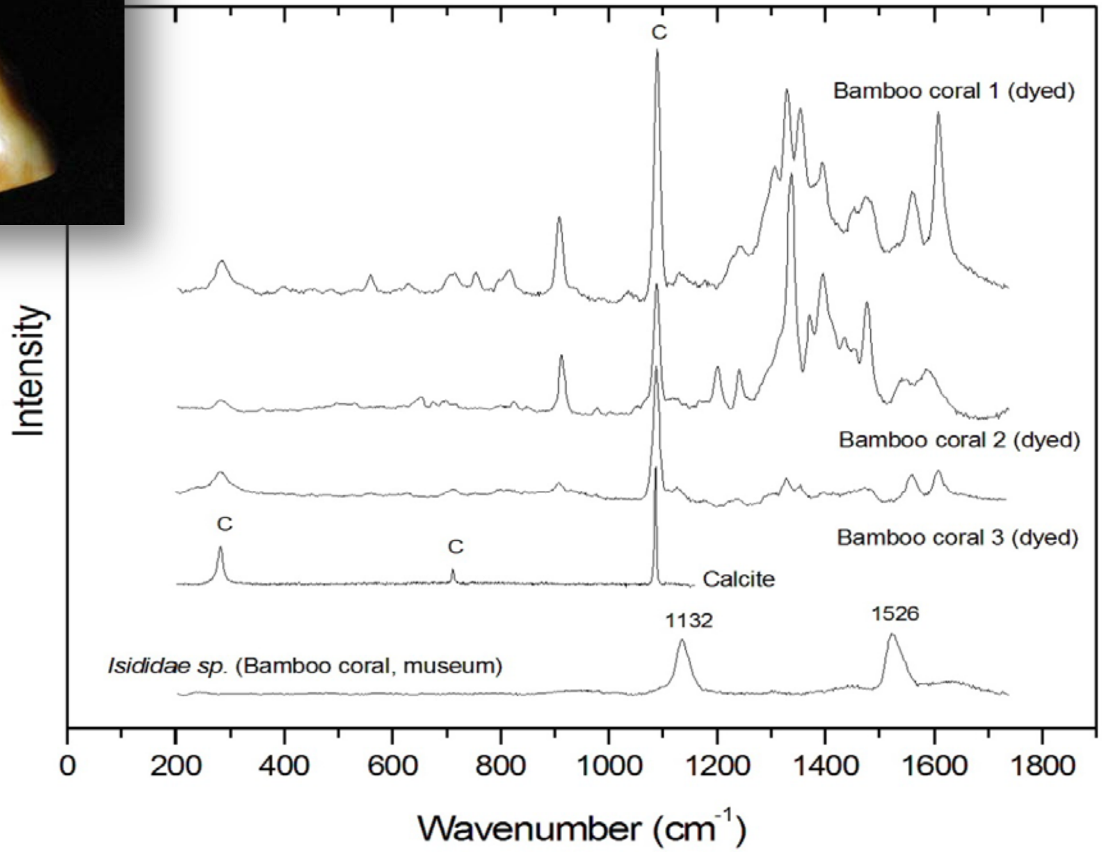
Ren Lu, GIA Laboratory, New York

- Freshwater “cultured” pink pearls, show the characteristic polyenic 1130-1530 cm^{-1} bands, large and asymmetric.
- No trace of dyes are found in freshwater white cultured pearls, while the resonance Raman spectrum of saltwater “white” pearls evidences the polyenic pigment.



A dyed “black” pearl shows the characteristic features of (amorphous) carbon at about 1350 and 1600 cm^{-1}.

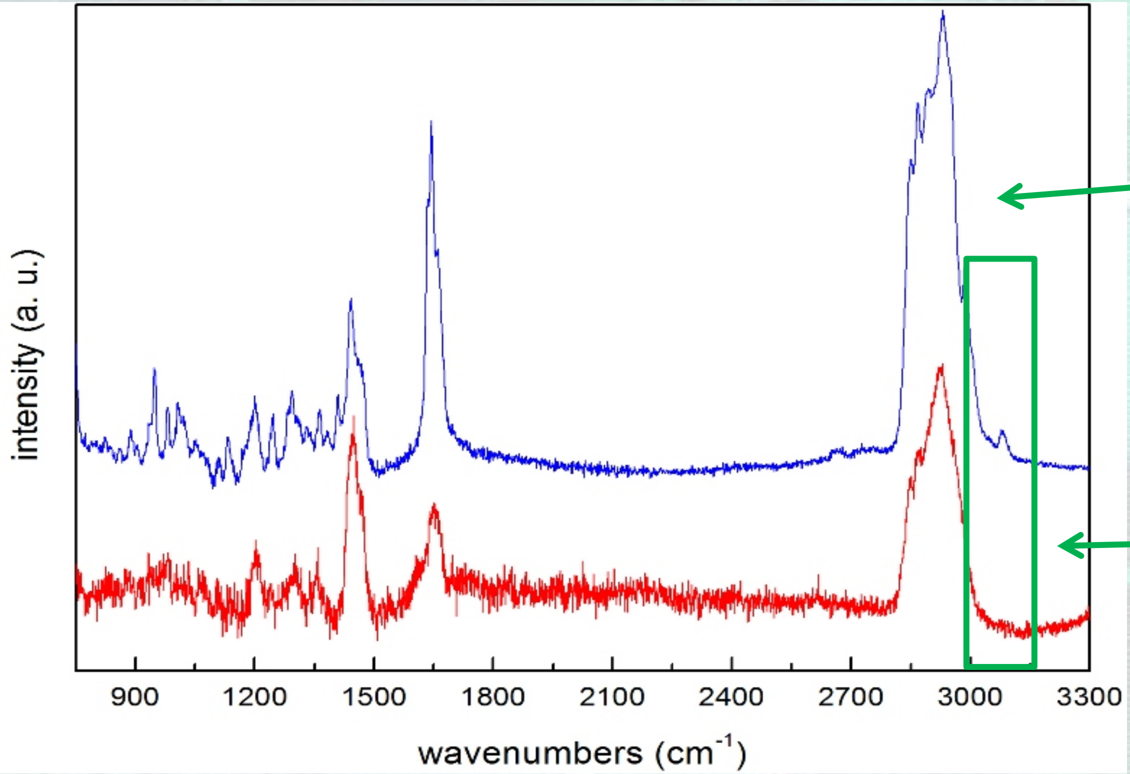
Organic gems: corals



Bamboo corals are generally artificially colored as evidenced by a comparison with natural *Isididae.*

Organic gems: amber and copal

- Peaks at 3080, 1645 and 887 cm^{-1} are attributed to the exocyclic methylene.
- They peaks can be used as indicators of the maturity level of the fossil resins: they appear at high intensity for copals but at low intensity for ambers



Copal (Madagascar)

Amber (Poland)

6) A CASE STUDY

The Garnet Group

$X^{2+}_3Z^{3+}_2(SiO_4)_3$

Pyrope

Almandine

Spessartine

Uvarovite

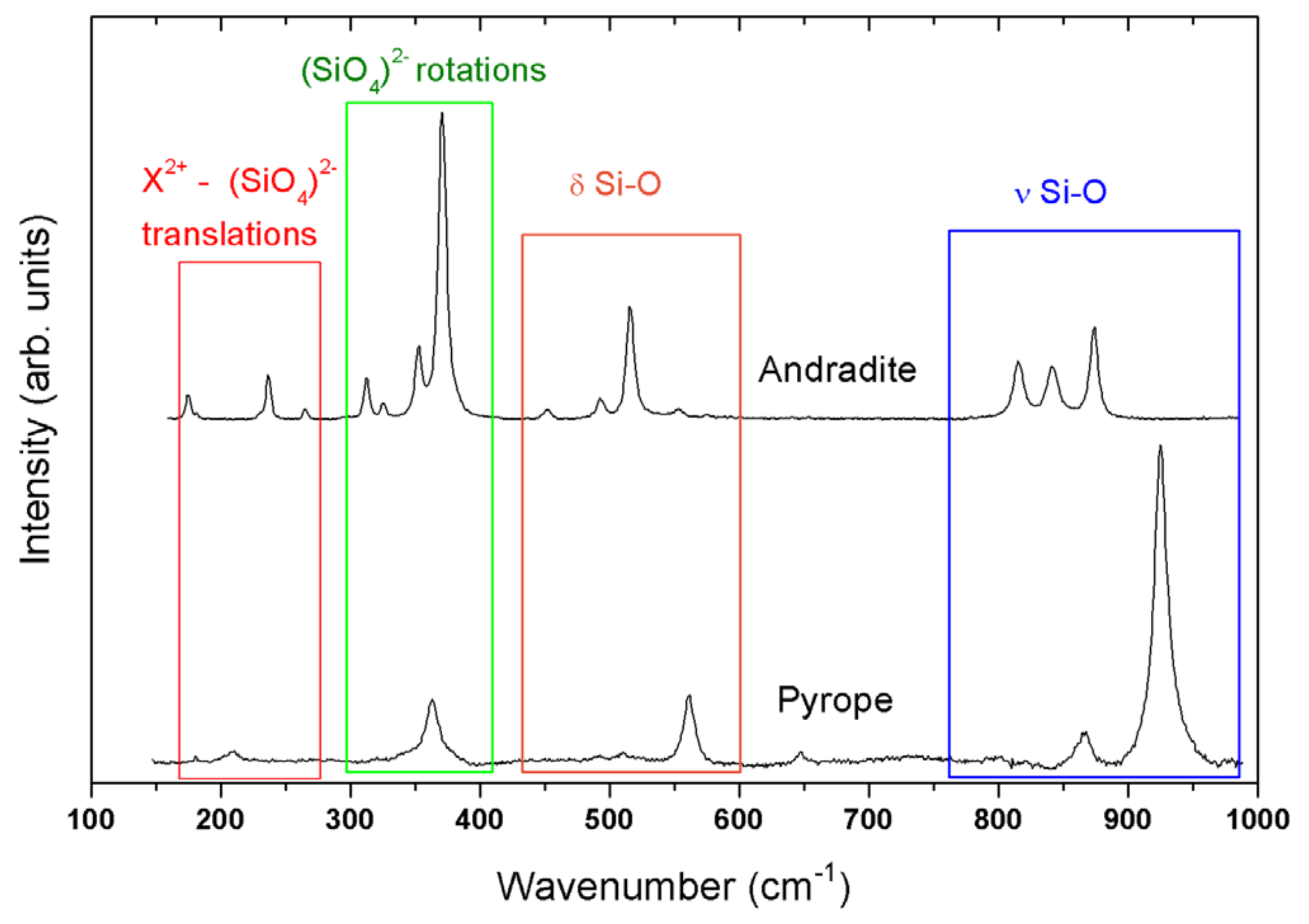
Andradite

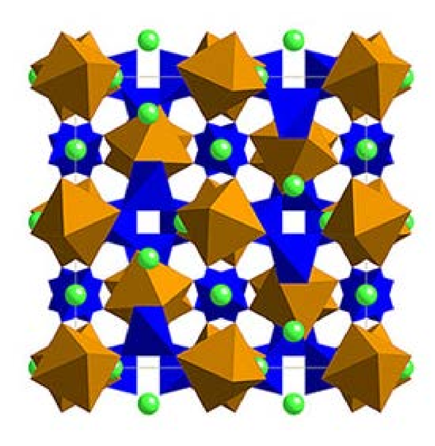
Grossular

Pyralspite family: Z = Al

Ugrandite family: X = Ca

The Raman spectra of garnets





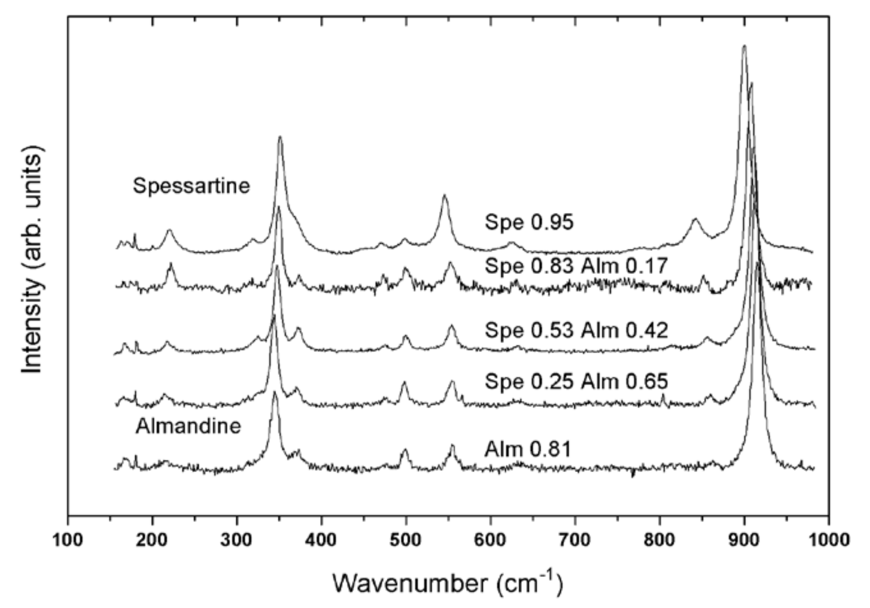
www.3dchem.com

The aim: to obtain the composition of natural garnets in terms of 6 end-members by means of micro-Raman spectroscopy

Linear approximation: for each band

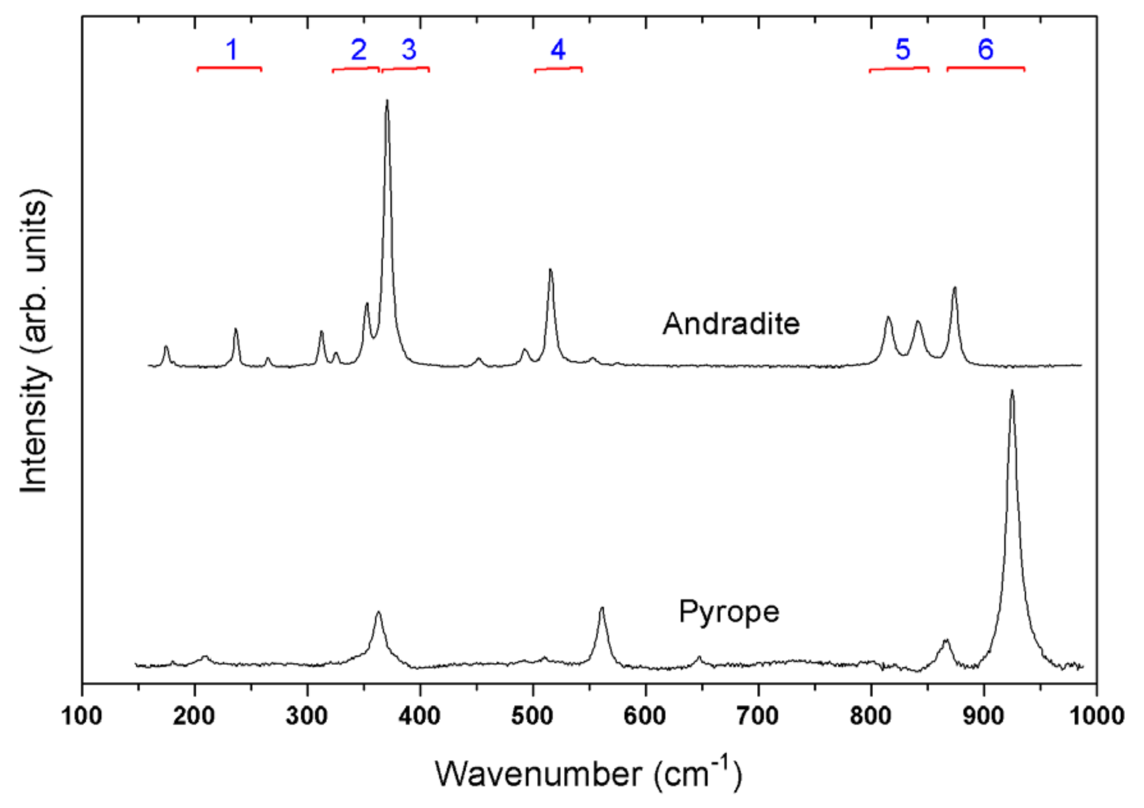
$$\begin{aligned}\nu = \; & x\mathrm{Alm}\cdot \nu\mathrm{Alm} + x\mathrm{Spe}\cdot\nu\mathrm{Spe} \\ & + x\mathrm{Pyr}\cdot\nu\mathrm{Pyr} + x\mathrm{Gro}\cdot\nu\mathrm{Gro} \\ & + x\mathrm{And}\cdot\nu\mathrm{And} + x\mathrm{Uva}\cdot\nu\mathrm{Uva}.\end{aligned}$$

If we know the frequency of 5 bands, we could obtain xAlm, Xspe…

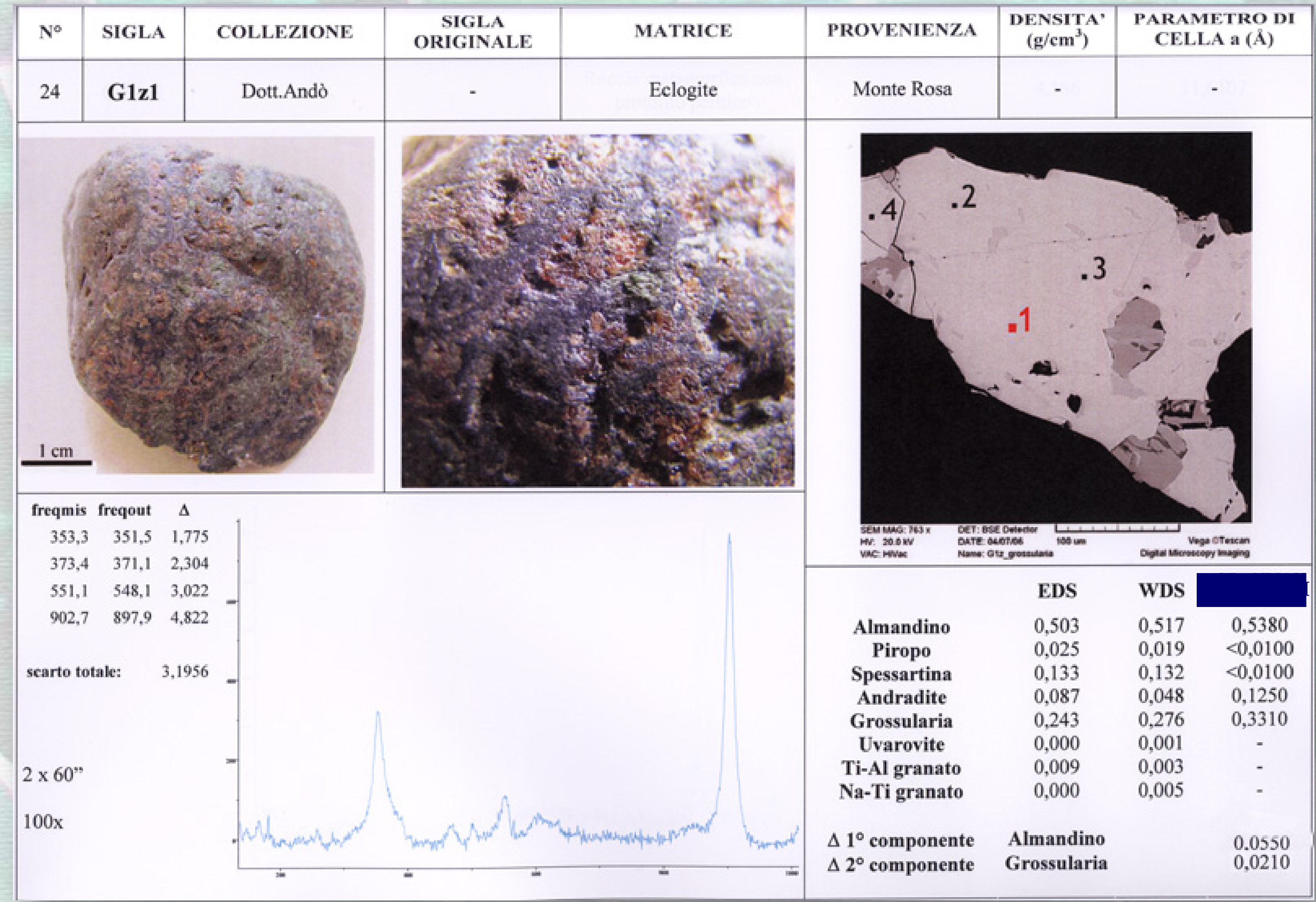


Choice of the peaks:

- Well visible in all the garnets
- Easy to identify
- With different trends to calculate the composition



Some Results



N°	SIGLA	COLLEZIONE	SIGLA ORIGINALE	MATRICE	PROVENIENZA	DENSITA' (g/cm^3)	PARAMETRO DI CELLA a (Å)
24	**G1z1**	Dott.Andò	-	Eclogite	Monte Rosa	-	-

freqmis	freqout	Δ
353,3	351,5	1,775
373,4	371,1	2,304
551,1	548,1	3,022
902,7	897,9	4,822

scarto totale: 3,1956

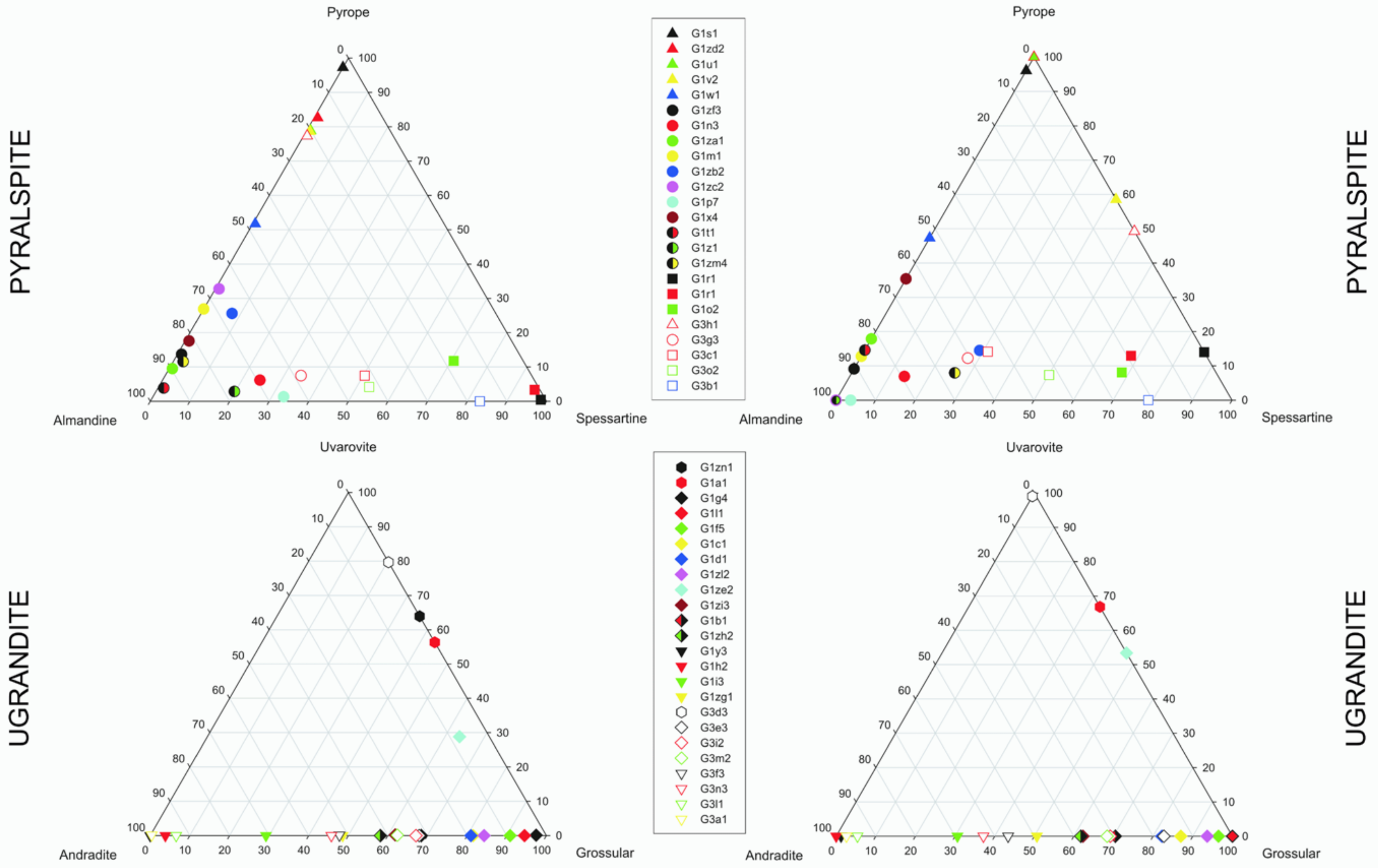
2 x 60"

100x

	EDS	WDS	[redacted]
Almandino	0,503	0,517	0,5380
Piropo	0,025	0,019	<0,0100
Spessartina	0,133	0,132	<0,0100
Andradite	0,087	0,048	0,1250
Grossularia	0,243	0,276	0,3310
Uvarovite	0,000	0,001	-
Ti-Al granato	0,009	0,003	-
Na-Ti granato	0,000	0,005	-
Δ 1° componente	Almandino		0.0550
Δ 2° componente	Grossularia		0,0210

WDS-electronmicroprobe analyses

Raman analyses

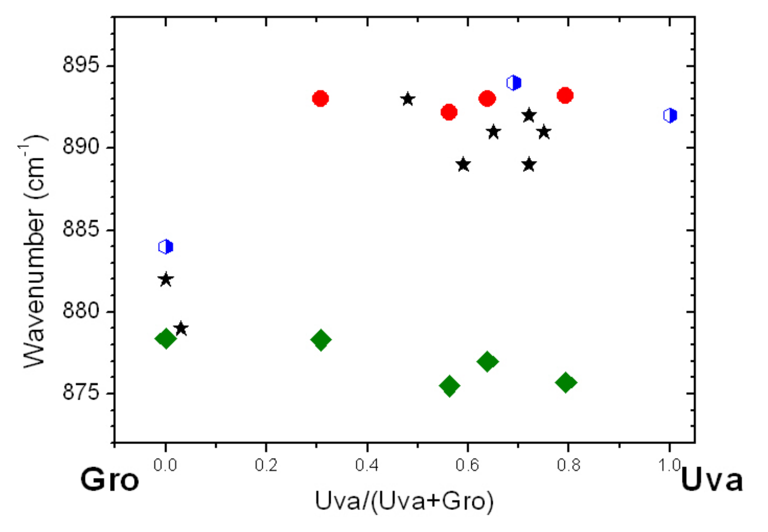


Problem: Uvarovite

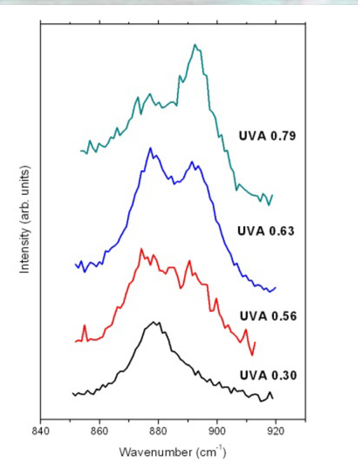
Literature:

- between 880-890 cm-1
- one-mode behaviour band

… or bimodal behaviour ?

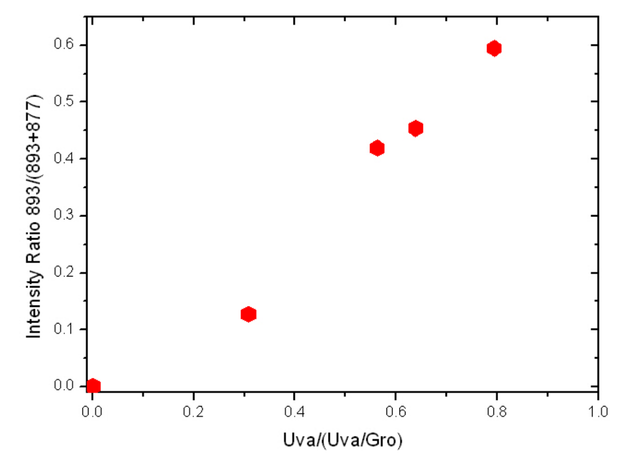


Cr^{3+} have a large crystal field stabilization energy – tighter bonds Influences also SiO4 stretching modes - higher frequencies



890/875 bands intensity ratio:

- bimodal behaviour
- useful tool to estimate uvarovite content



The new version (MIRAGEM 2)

- No minimization process: all compositions tested
- No need to solve the doublet at 370 cm^{-1}
- Attempt to correct badly calibrated spectra
- Automatized I/O of tables of Raman data

To test it, please ask me (danilo.bersani@fis.unipr.it)

Conclusions 1

Raman Spectroscopy in gemology is able to give some answers about:

- **Identification**
- **Composition**
- **Natural/synthetic origin**
- **Provenance and genesis**
- **Purity**
- **Presence of enhancements**

Conclusions 2: about database

- **Orientation:**
    - **disappearance of some peaks**
    - **fake shift**
- **Resonance:**
    - **change in intensities and shift**
- **Fluorescence:**
    - **include or exclude the PL bands?**
    - **es. doublet of Cr in Al_2O_3 is diagnostic @ 632 nm**

Conclusions 2: about database

- Disorder
    - New “disorder” bands
    - Shifts and broadening
- Use of the “gem” name?
    - Minerals belonging to a series (es. garnets, tourmalines; olivines)
    - Gems from different families (es. jade)
- Attention to avoid peaks of abrasives, resins, fillers, inclusions, neon…

Thank You

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Analysis of glass artefacts: applicability of XRF, SEM/EDX, FTIR, and Raman

Manfred Schreiner

Dubravka Jembrih-Simbuerger

Academy of Fine Arts, Vienna, AT

THURSDAY, SEPTEMBER 27: LECTURE 7

IRUG-Workshop, Sept. 27 – 29, 2012

Analysis of Glass Artefacts

~

Applicability of XRF, SEM/EDX, FTIR, and Raman

Manfred Schreiner
Dubravka Jembrih-Simbürger
Institute of Science and Technology in Art
Academy of Fine Arts Vienna/Austria
www.ntk.akbild.ac.at

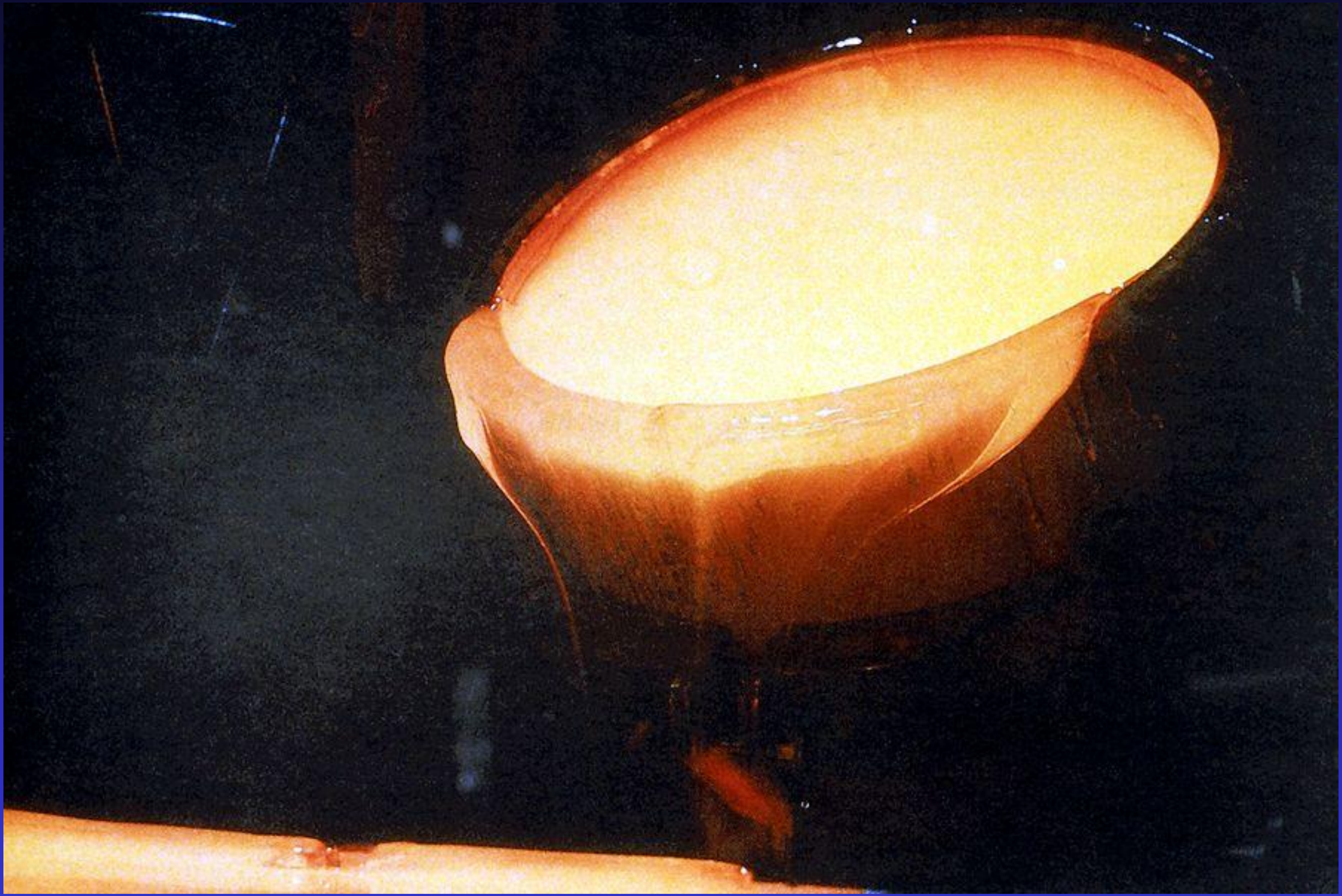
Glass – more than 4000 years

Technology for glass production:

Ancient and Modern Glass

Sand + Soda (Natron) + Chalk (Lime)

$SiO_2 + Na_2CO_3 + CaCO_3$



Glass Melt → soda – lime - silica glass

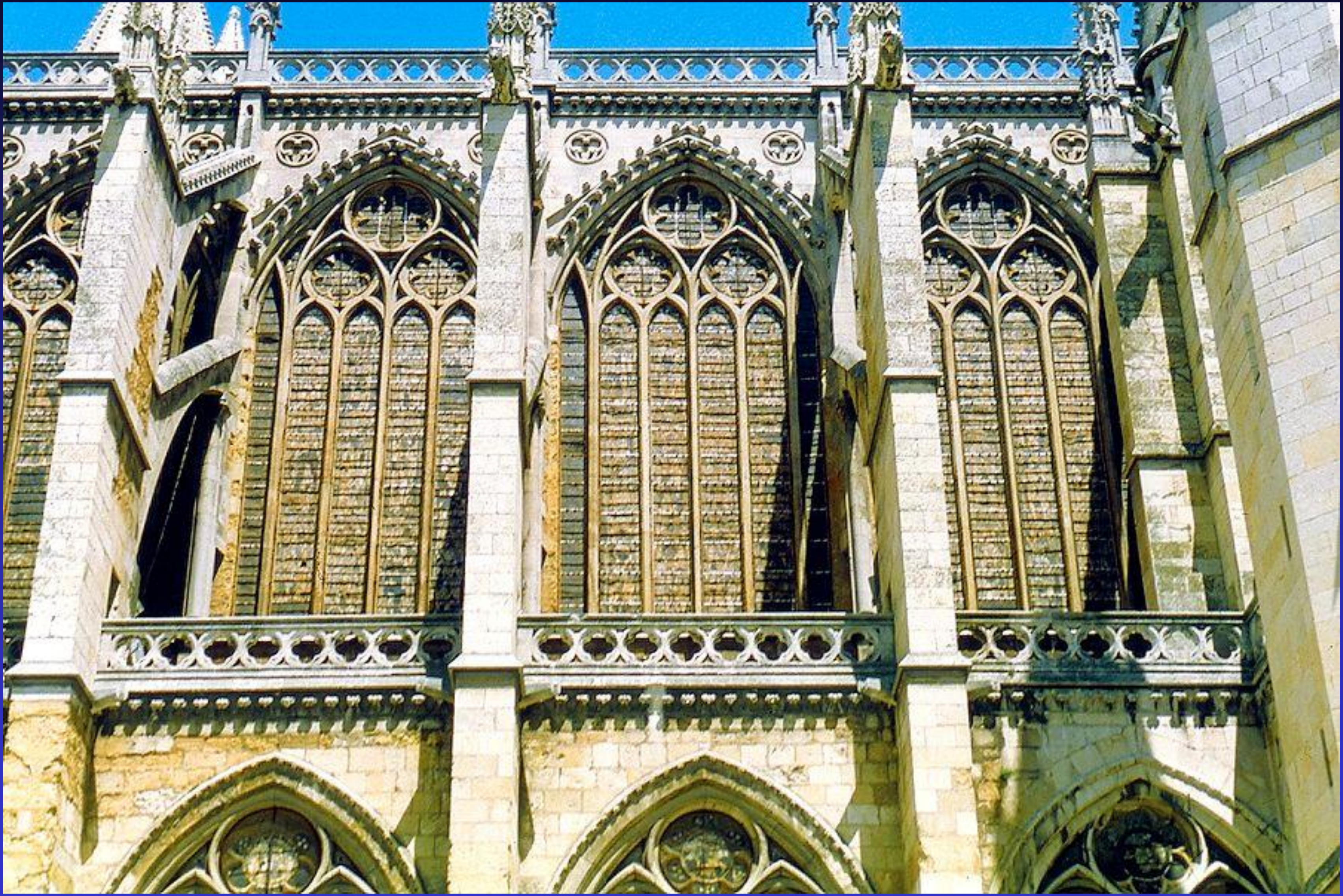
Glass – 4000 years

Medieval Glass (North of the Alps)

Sand + Potash + Chalk

SiO_2 + K_2CO_3 + $CaCO_3$

→ potash – lime - silica glass



Aim of scientific investigation

- **Glass Composition** → authenticity

  Where, when and by whom was an object made ?

  How was the manufacturing procedure ?

- **Glass Degradation** → conservation

  Condition of an artifact (state of preservation)

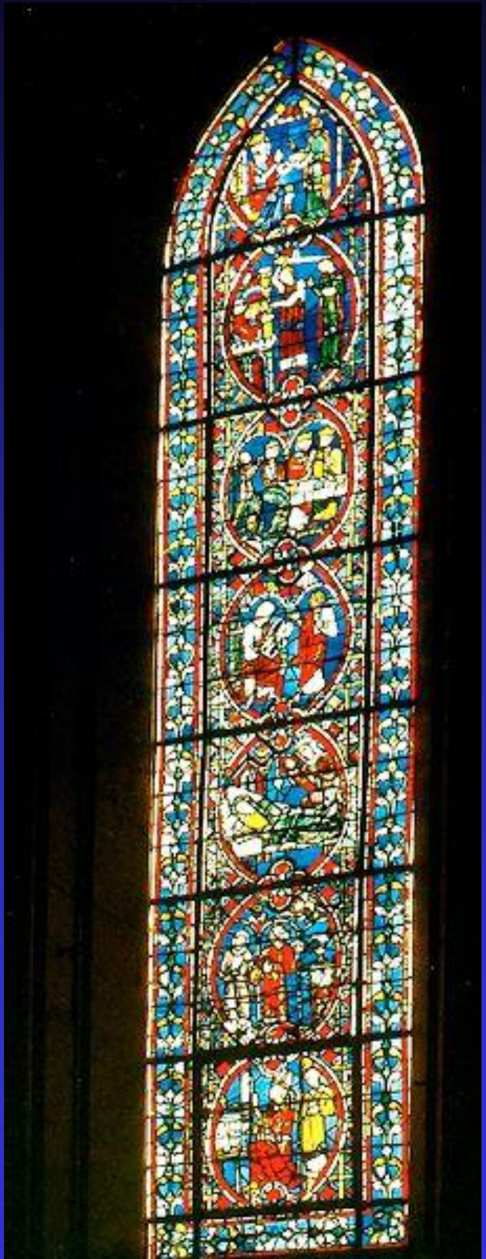
  Conservation/restoration treatment

Requirements for the Analysis of Artifacts

- **non-destructive analysis (non-sampling)**
- **air path system (no vacuum !!)**
- **transportation of the artefact / instrument**
- **surface (patina) and bulk analysis**
- **fast**
- **costs**

Iridescent glass of the Art Nouveau:
Tiffany/USA or
Loetz/Austria,
beginning of 20th cent.

Archaeological glass of Ephesos/Turkey

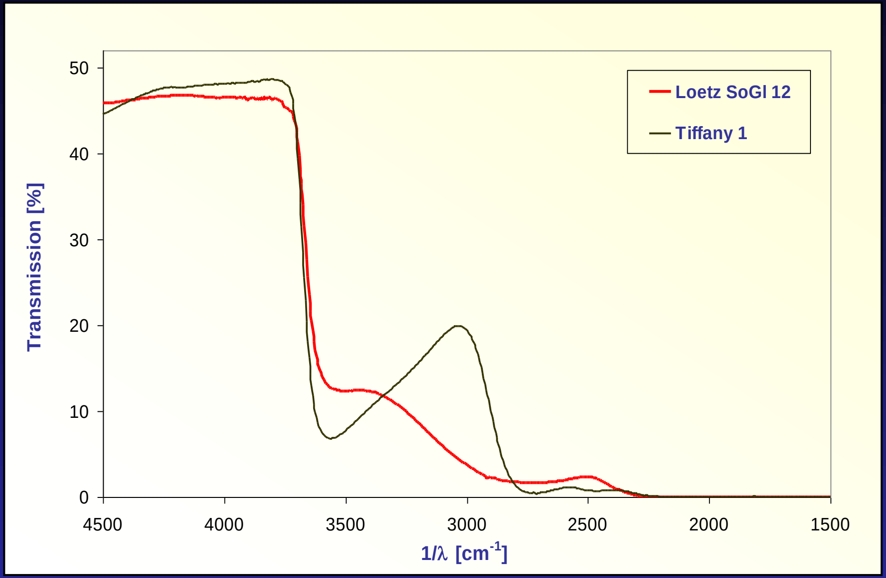


Medieval stained glass

Iridescent Art Nouveau glass of *Tiffany* and *Loetz*

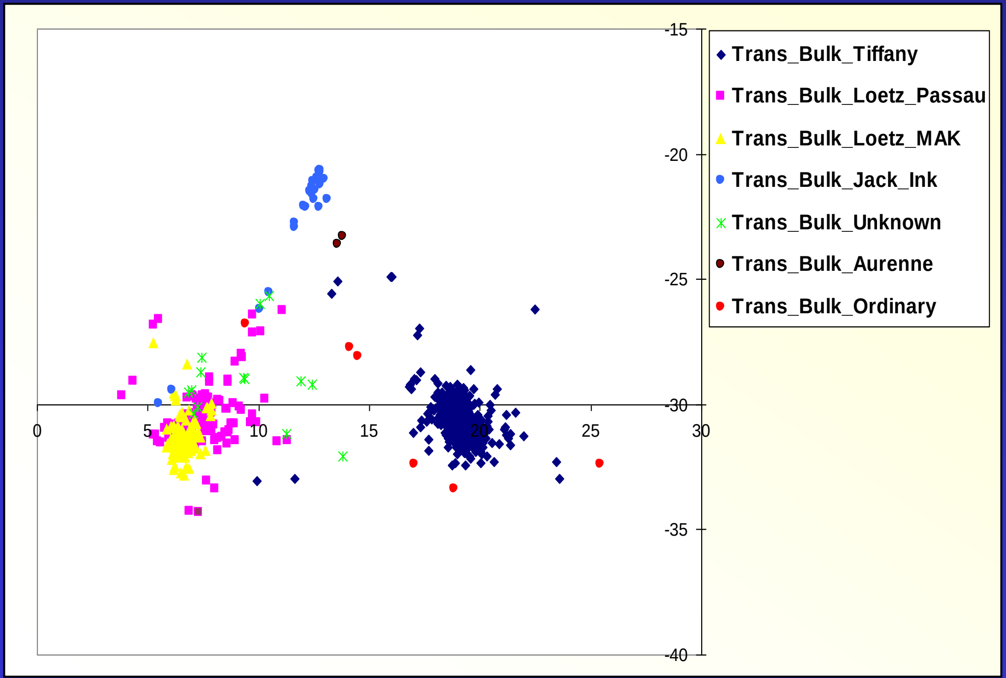
Characterization of the provenance (authenticity) of an object

XRF, SEM/EDS, FTIR, Raman



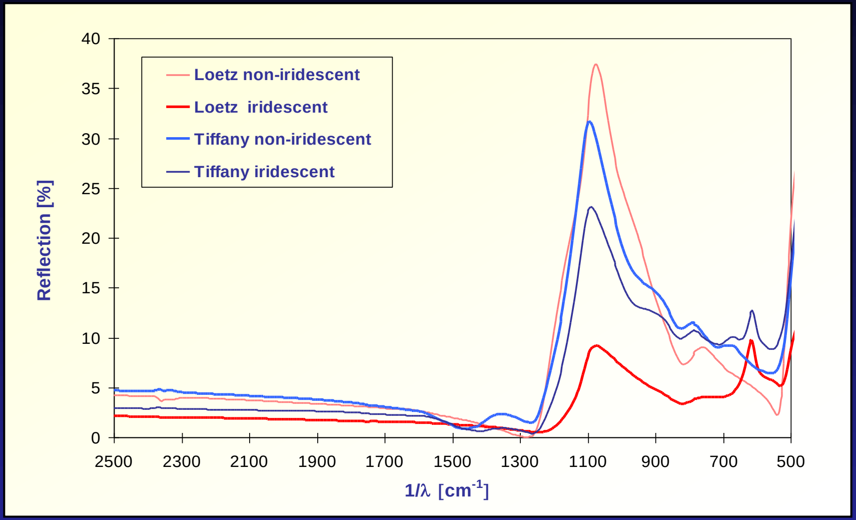
FTIR

Example of **transmission spectra** of Loetz and Tiffany glass fragment (30 scans, resolution: 4 cm^{-1})

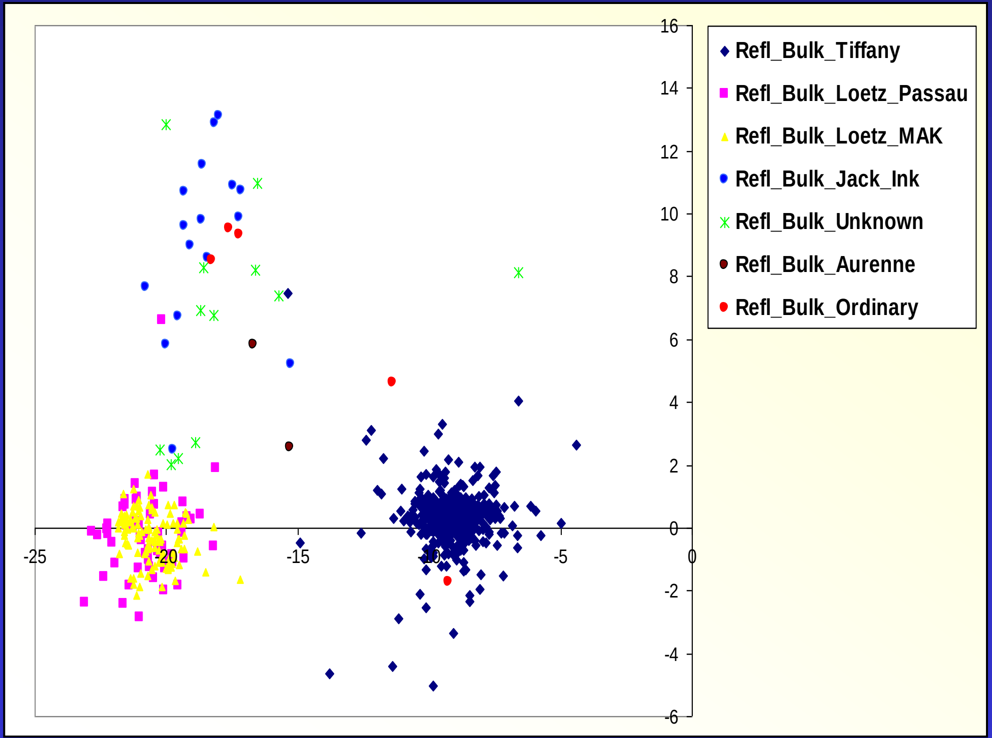


Multivariate statistical data evaluation

(Scatter plot of canonical variate analysis of **transmission data)**



Example of **reflection spectra** of Loetz and Tiffany glass fragment (30 scans, resolution: 16 cm^{-1})



Scatter plot of canonical variate analysis of **reflection data**

Raman Spectroscopy of Glass

- Study of glass structure using Raman scattering began in the 1950s

- Since its development in 1960s

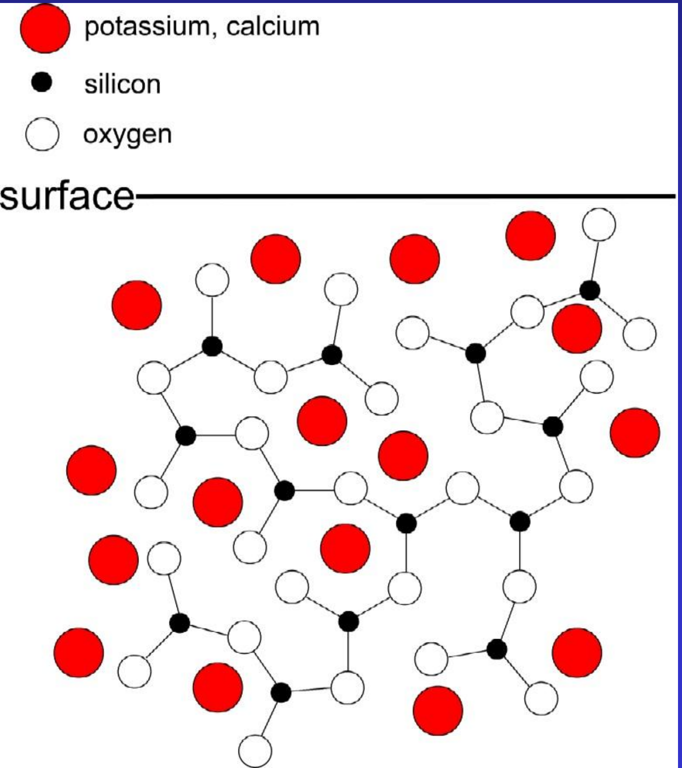
↓

Laser Raman spectroscopy has been used as one of the major tools for studying glass structure

- the vibrational spectra of inorganic glasses depend mainly on the network structure

⇓

glass-formers are the principal factor determining their vibrational spectra - **the effect of ions outside the network is secondary**



⇒ SiO_4-tetrahedra (network former)

⇒ bridging (BO) and non-bridging oxygen (NBOs)

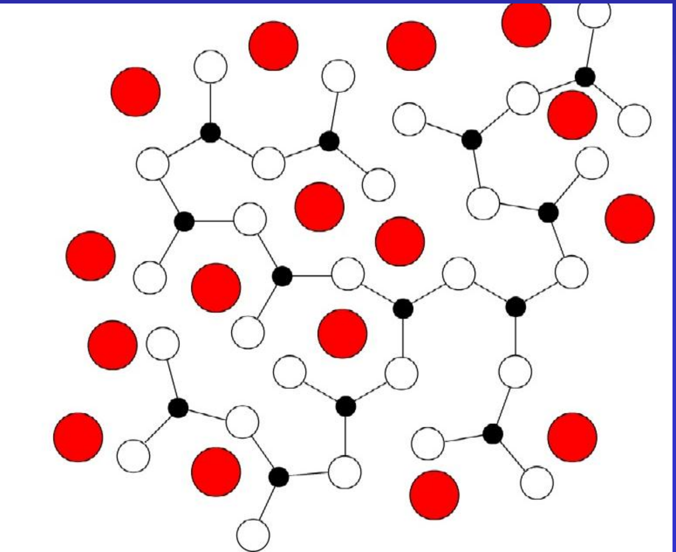
⇒ Na, K, Ca, Mg etc (network modifiers)

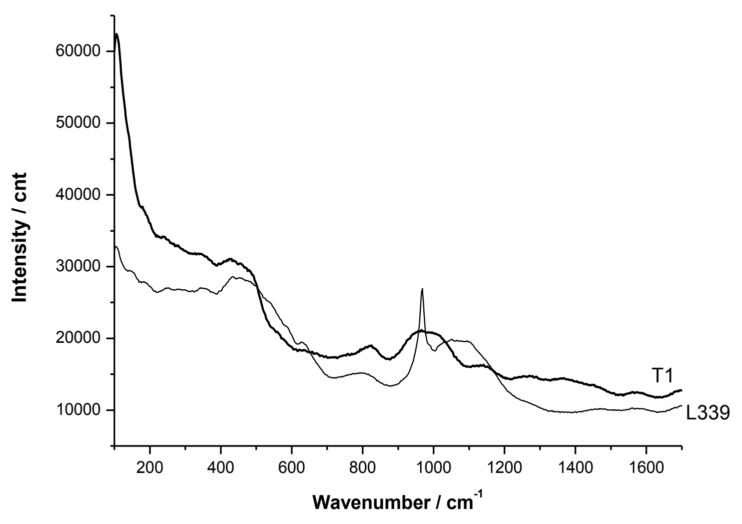
- the states in which each chemical bond is situated are not the same due to the

long-range disorder of glass structure

⇓

this broadens the vibrational spectral peaks into bands for each chemical bond in the network structure





Raman applications in the field of glass in cultural heritage

- **Determination of glass composition**

- Iridescent Art Nouveau glass
- Identification of glassy silicates used in ceramics, glass and jewellery (*Ph. Colomban et al.*)
- Identification and dating of ancient/modern stained glasses (*Ph. Colomban et al.*)

➢ Investigations of the glass degradation

- Alteration of historic glasses by acidic pollutants *(L. Robinet et al., JRS)*
- Raman spectroscopy for predicting stability of historic glasses *(L. Robinet et al., JRS)*
- Raman identification of ancient stained glass and their degree of deterioration *(Ph. Colomban et al., JRS)*

Raman spectroscopy on glass / instrumentation

- Non-destructive
- Laboratory and portable instruments
- Surface sensitive
- Laser sources: **514** and **532 nm**
- Laser power @ the sample typically 1- 40 mW

- **Laboratory instruments** coupled to microscopes

⇓

μ-Raman instrumentation

confocal – information from “different layers”

Glass

- **corrosion products at the surface**
- **leached layers / iridescent surface**
- **bulk**

- **Portable Raman instruments (on-site measurements)**

- with optic fibers / focus objective
- useful for objects with different forms and shapes – **glass artefacts**

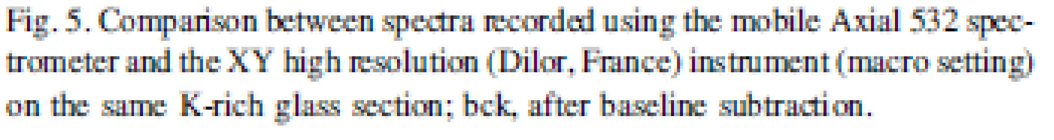
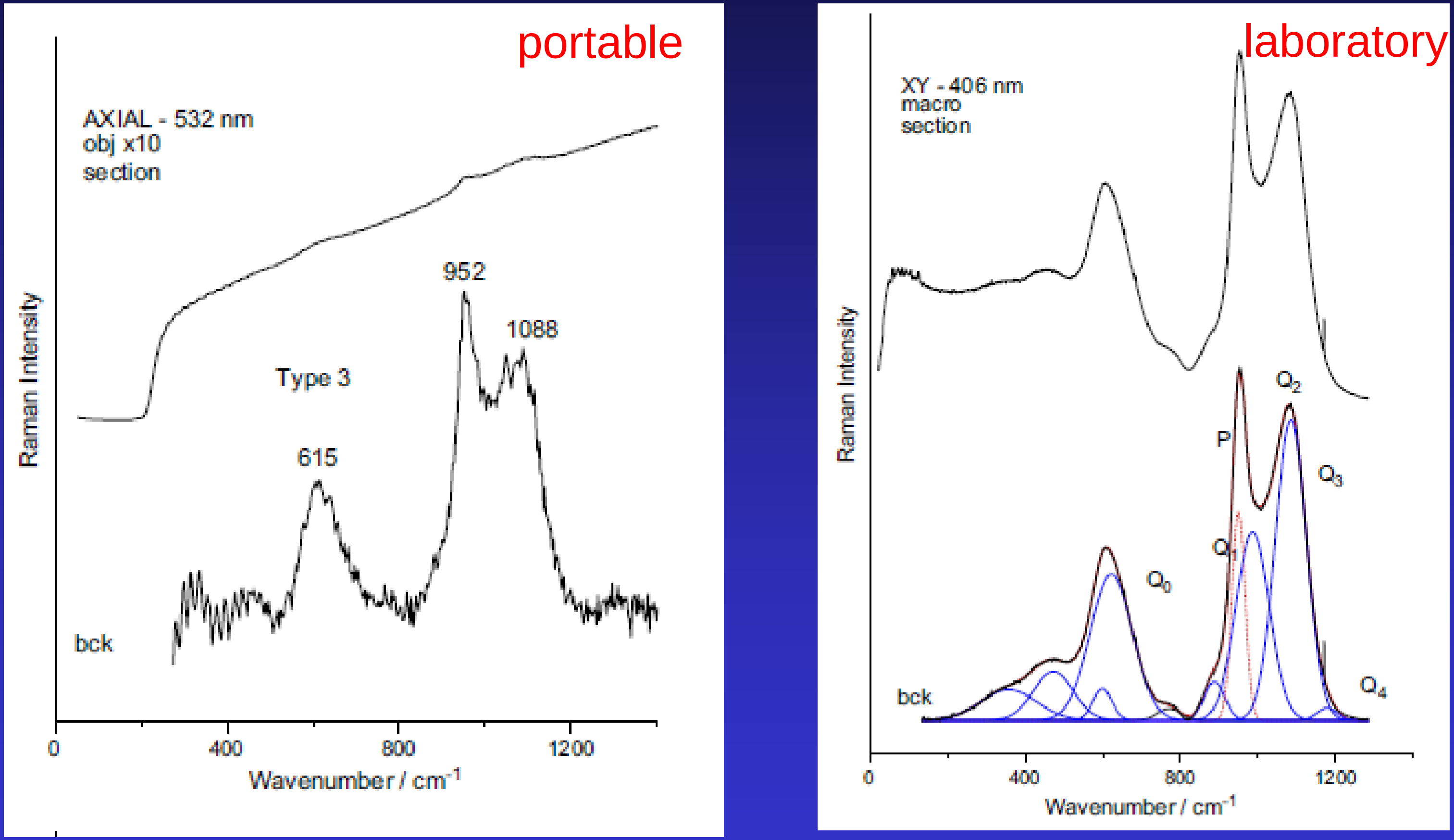


Fig. 5. Comparison between spectra recorded using the mobile Axial 532 spectrometer and the XY high resolution (Dilor, France) instrument (macro setting) on the same K-rich glass section; bck, after baseline subtraction.

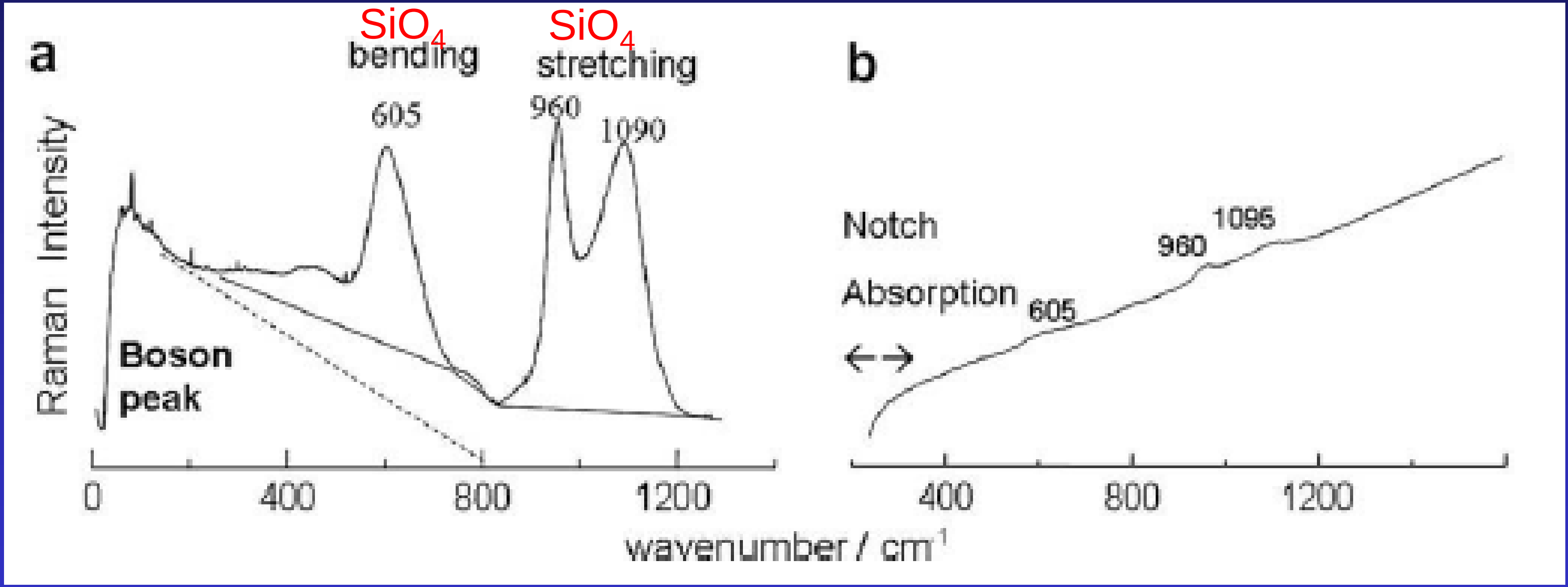


Ph. Colomban, A. Tournie: Journal of Cultural Heritage 8 (2007) 242 – 256. Fig. 5

Data evaluation

1. Baseline subtraction

Boson peak: combination of librations of SiO_4 tetrahedra and localized vibrations of network-modifying cations with NBOs



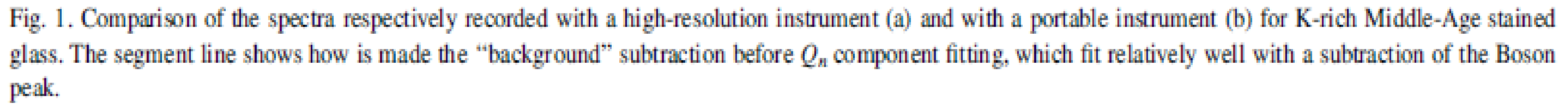


Fig. 1. Comparison of the spectra respectively recorded with a high-resolution instrument (a) and with a portable instrument (b) for K-rich Middle-Age stained glass. The segment line shows how is made the "background" subtraction before Q_n component fitting, which fit relatively well with a subtraction of the Boson peak.

Ph. Colomban, Journal of Cultural Heritage 9 (2008) e55-e60

2. **Calculation of spectral components Q_n and peak fitting:**

Decomposition of the spectra into their Q_n (n= number of bridging O) components representative of different arrangements of the tetrahedra within the polymerized Si-O network

Ph. Colomban, A. Tournie, L. Bellot-Gurlet, J. Raman Spectrosc. 37 (2006) 841-852:

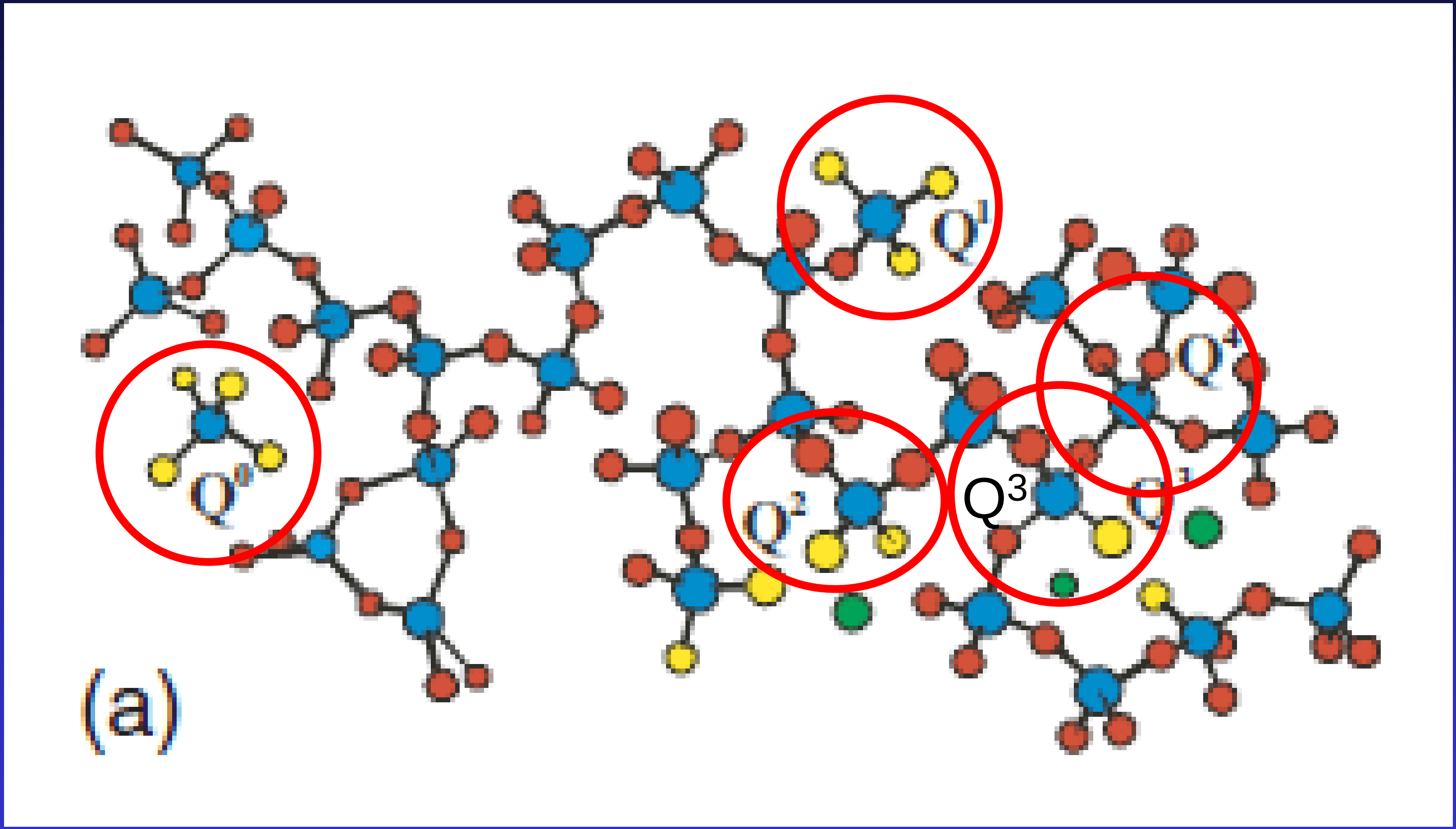
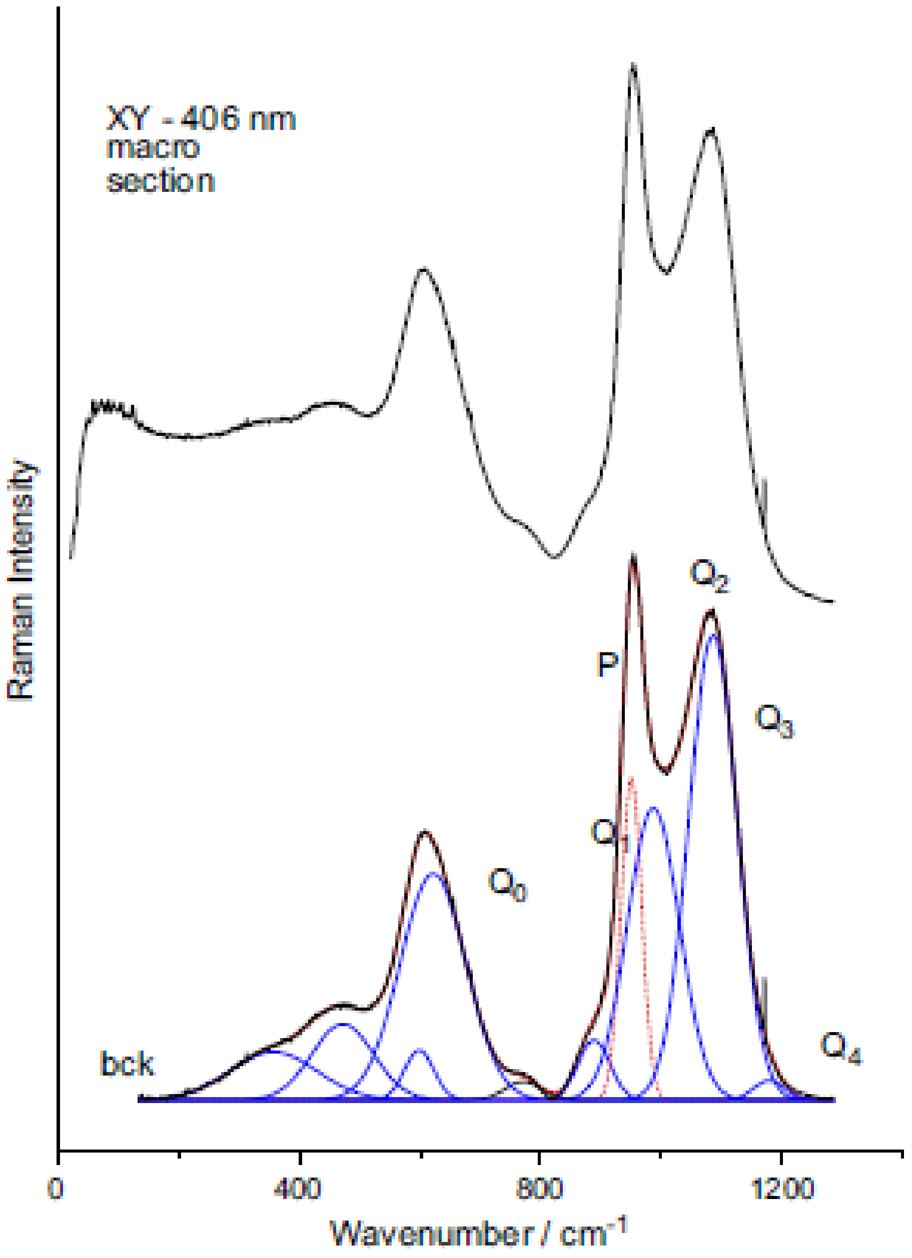


Figure 1. (a) Schematic diagram of the SiO$_4$ polymerised network of a glassy silicate; isolated (Q$_0$), connected with one (Q$_1$), two (Q$_2$), three (Q$_3$) and four (Q$_4$) Si–O–Si bridge tetrahedra are indicated.


XY - 406 nm
macro
section
Raman Intensity
P
Q2
Q3
Q1
Q0
bck
Q4
0
400
800
1200
Wavenumber / cm-1

3. **Calculation of polymerization index I_p:**

Ratio Areas Si-O bending multiplet versus
Areas Si-O stretching ($I_p=A_{500}/A_{1000}$)

In General:

According to the position, relative intensity and shape of the Raman bands

⇩

Differentiation between different compositions

or

the same composition but different nanostructures

4. **and/or Multivariate data analysis**

- Cluster analysis
- Principal component analysis (PCA)

Case studies - Identification, dating, determination of glass provenance

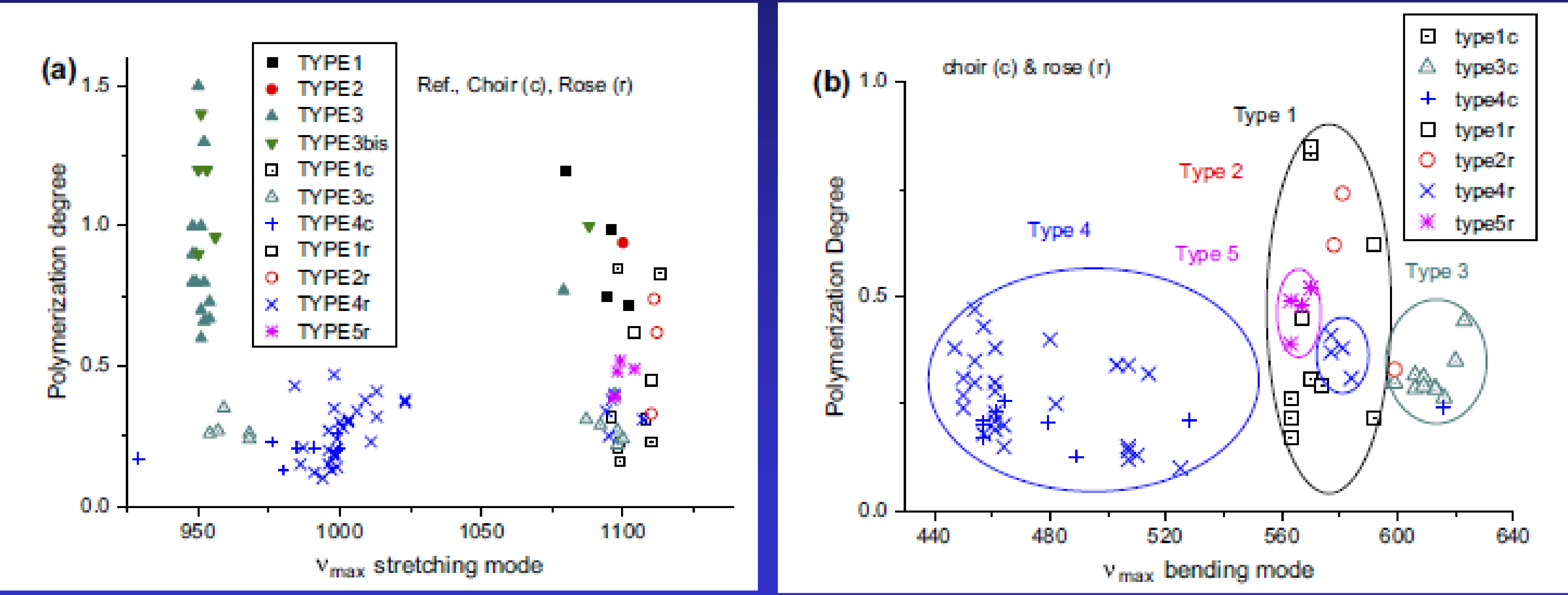
1. On-site Raman **identification and dating of ancient/modern stained glasses** at the Sainte-Chapelle, Paris

Ph. Colomban, A. Tournie: Journal of Cultural Heritage 8 (2007) 242 – 256.

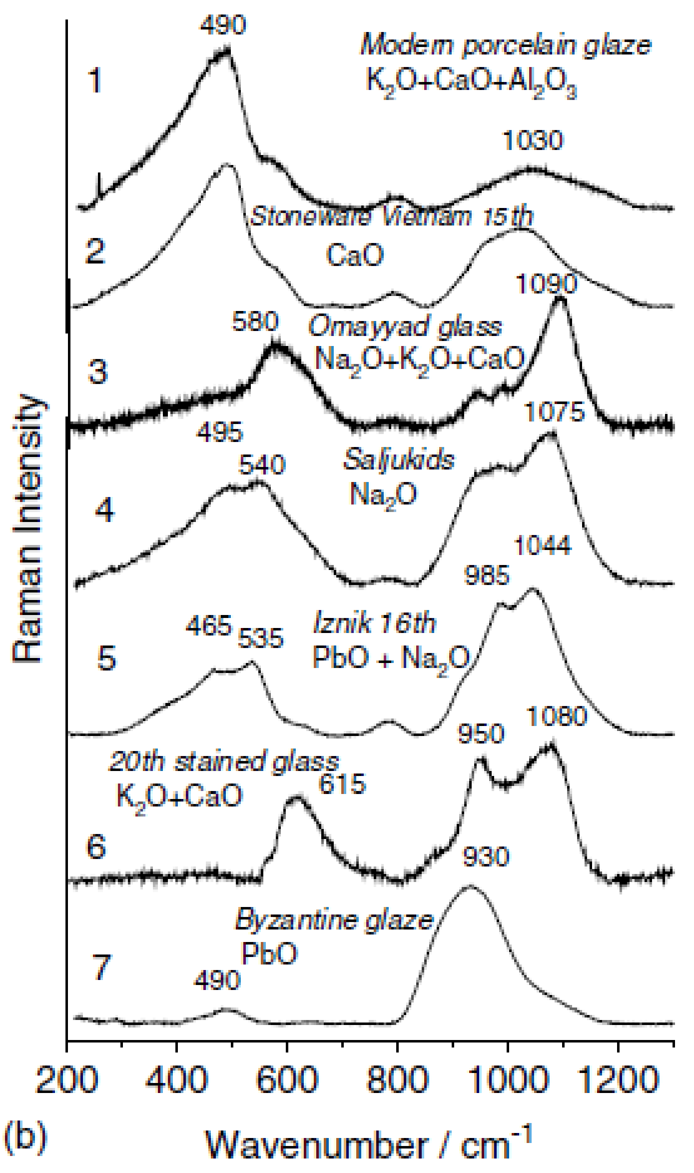
- Stained glass windows

- Some of them were damaged during/after the French revolution, partly restored in the 19th century

Type 1: Ca-Na silicate (19th century productions)
Type 2: Na-Ca silicate (19th century productions)
Type 3: K-Ca silicate (medivial glass)
Type 4: strongly weathered Type 3



Ph. Colomban, A. Tournie: Journal of Cultural Heritage 8 (2007) 242 – 256. Fig. 8



2. Glassy silicates used in ceramics, glass and jewellery

Ph. Colomban, A. Tournie, L. Bellot-Gurlet: J. Raman Spectrosc. 37 (2006) 841-852

Fig. 4 (b): Representative Raman spectra for the 7 families identified

baselines have been subtracted

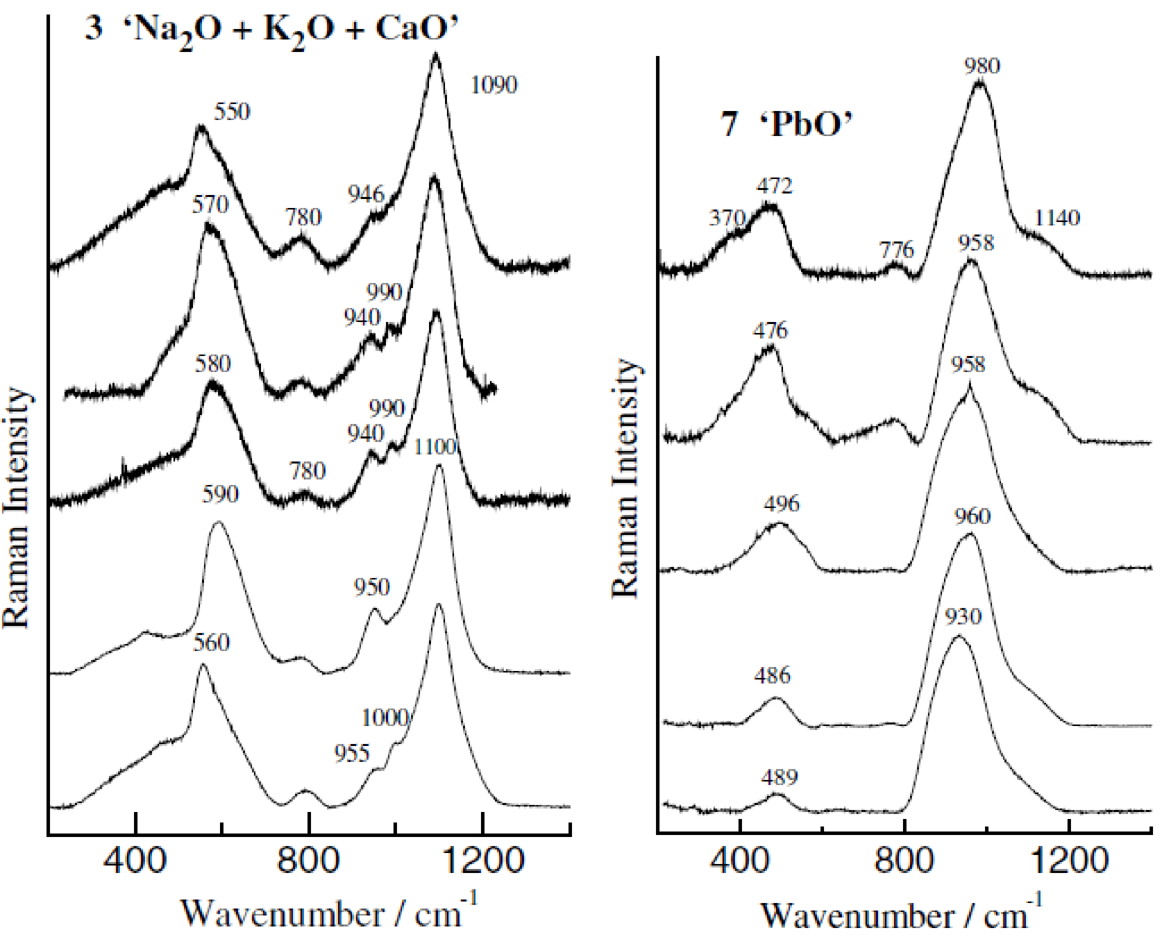


Figure 8. Example of Raman signatures (families 3 and 7).

➡ $I_p = A_{500}/A_{1000}$

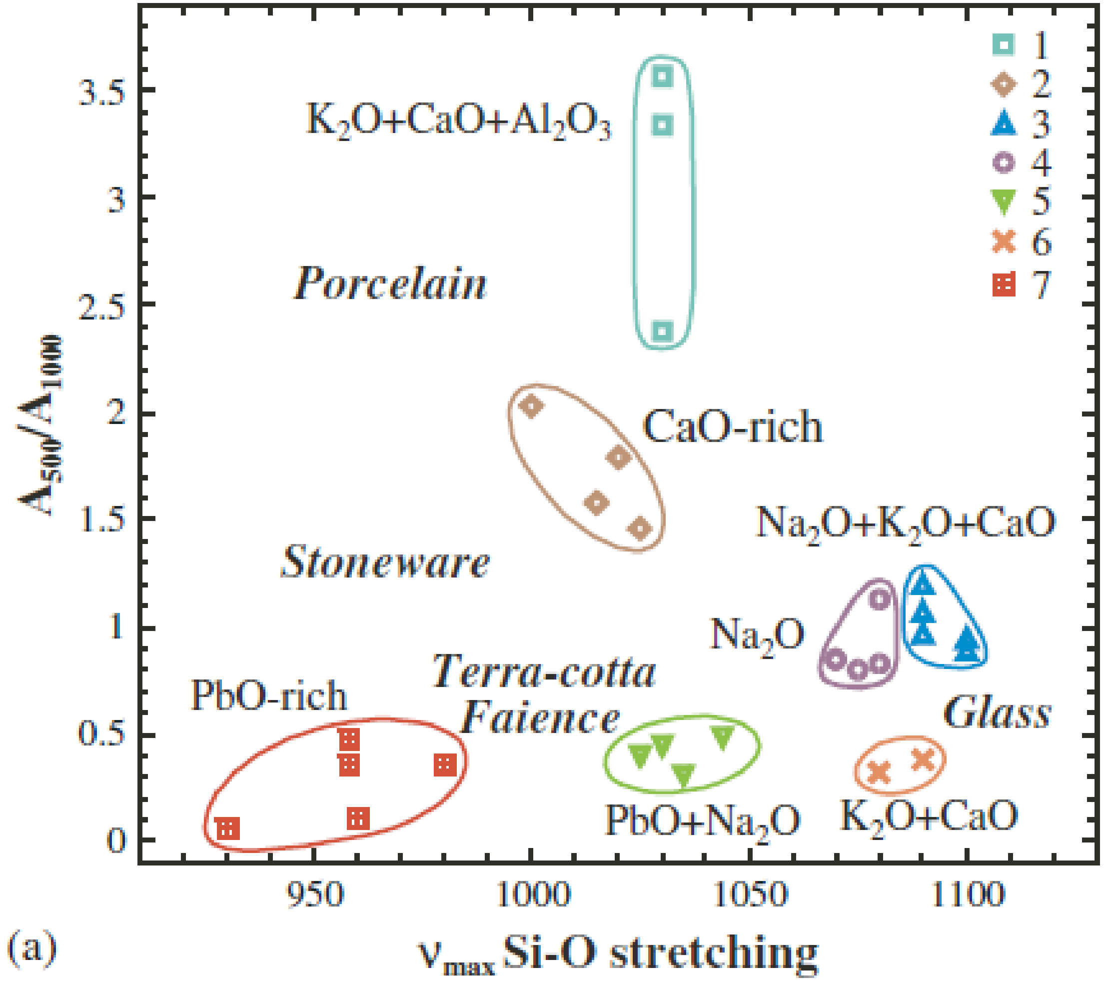


Figure 9. Plots of the polymerisation index as a function of the main Si–O stretching component wavenumber (a)

and/or

- Cluster analysis,
- Principal component analysis (PCA)

3. **Iridescent Art Nouveau Glass**

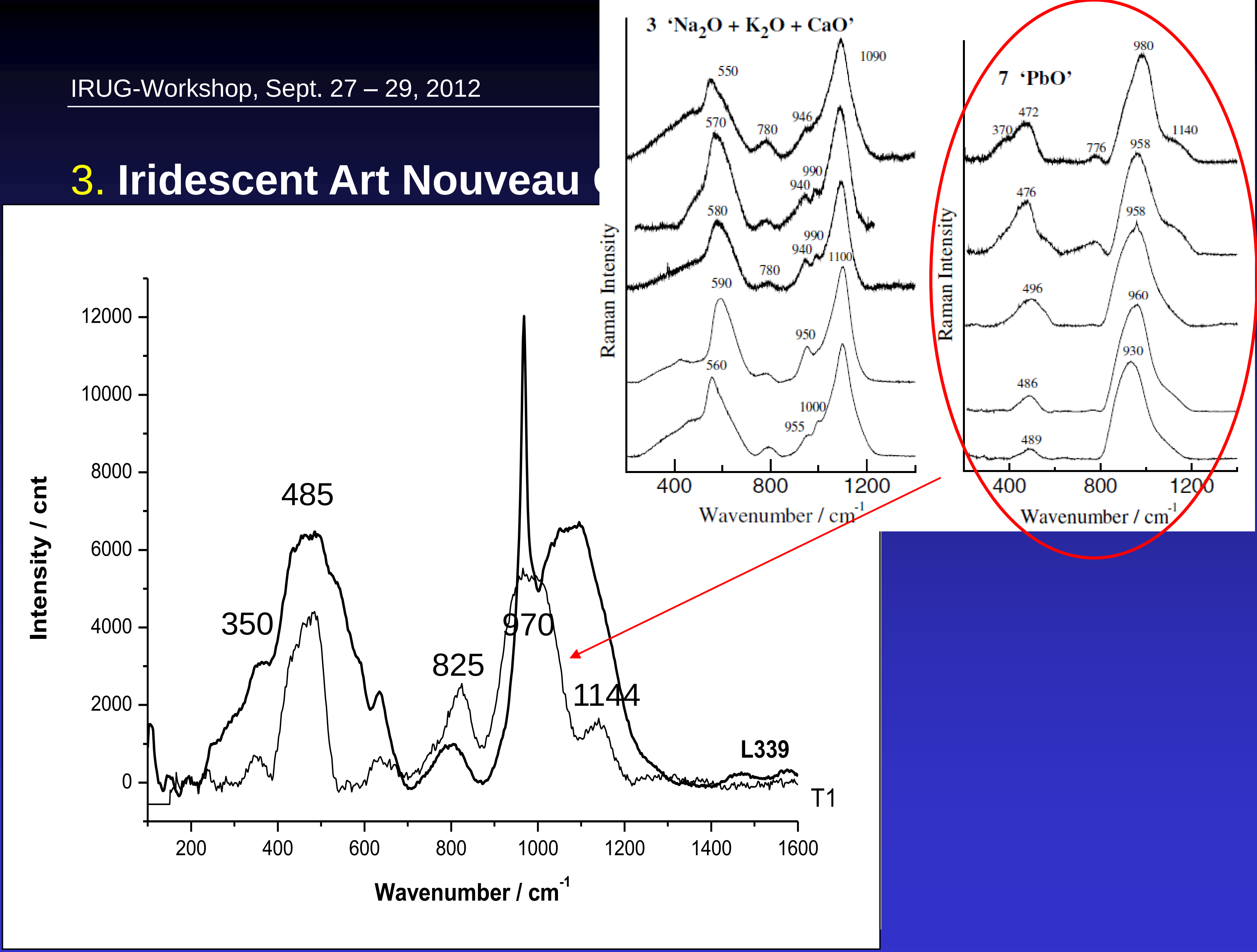
- Iridescent glass fragments manufactured by

  Tiffany (lead silicate) and Loetz (K-Ca-silicate)

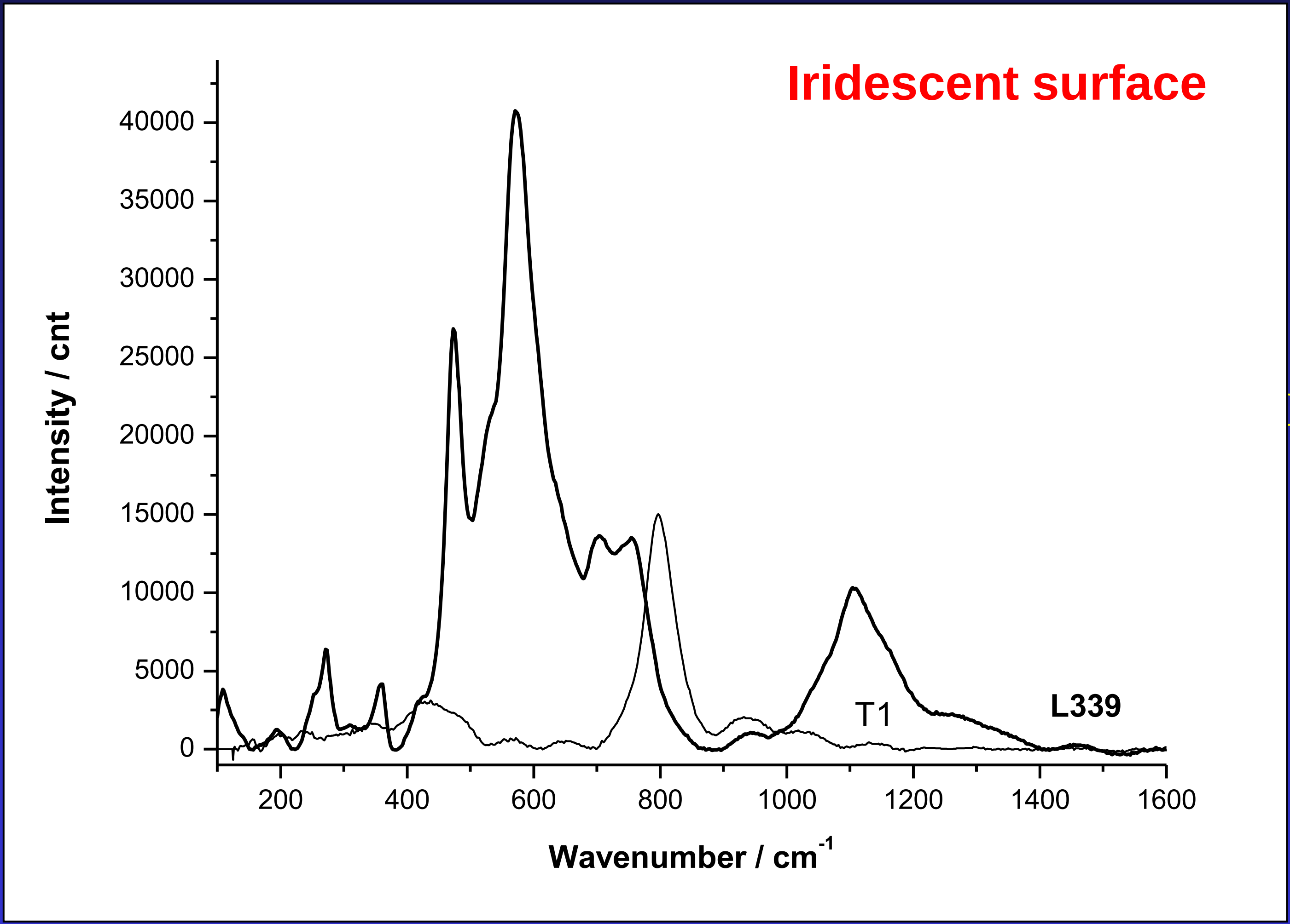
- ***Bulk glass / overlay of Loetz is sensitive to the laser power***, shorter measuring times necessary, measuring parameters has to be adjusted from glass to glass

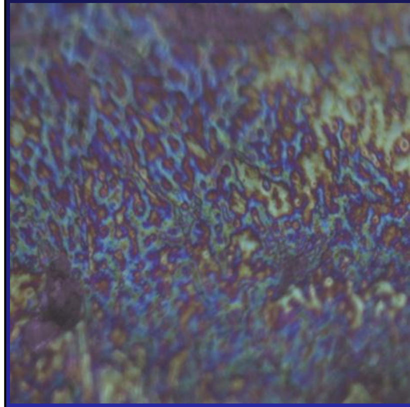
- Different measuring parameters were considered (variation of the confocal hole, objective magnification, laser power, measuring time etc.)

3. Iridescent Art Nouveau

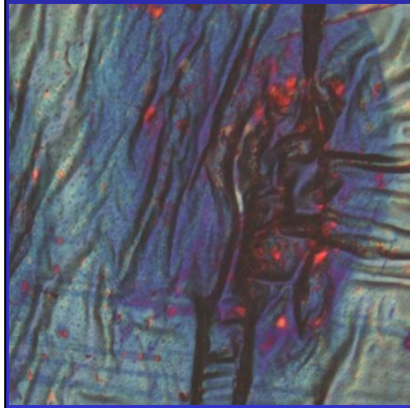


3. Iridescent Art Nouveau Glass





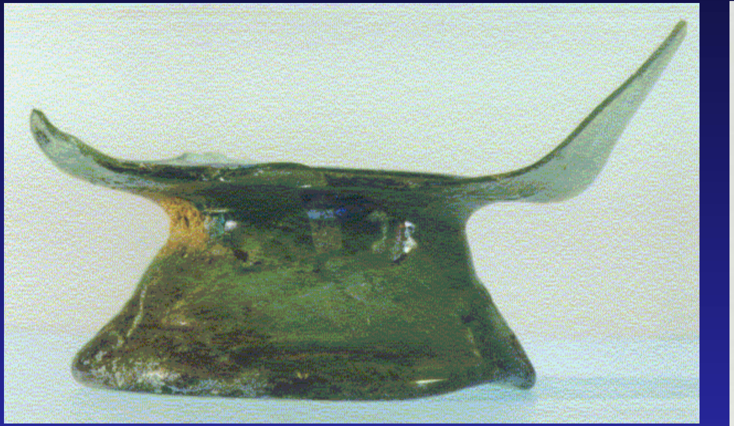
L339 irid. 50xlwd



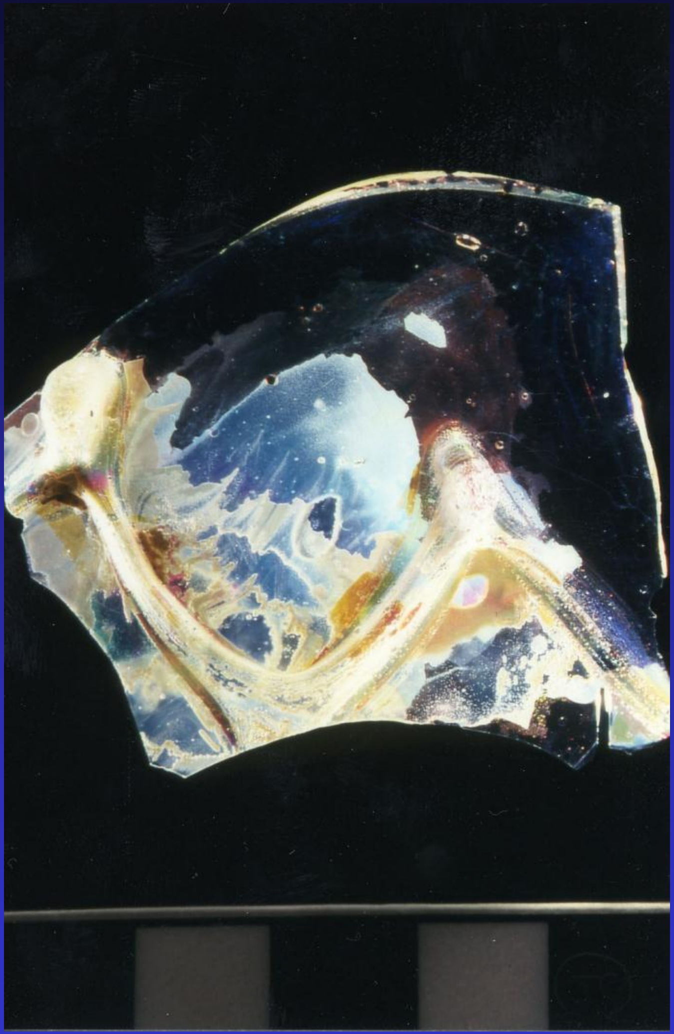
T1 iris 50xlwd

Glass degradation

Glass of Ephesos/Turkey

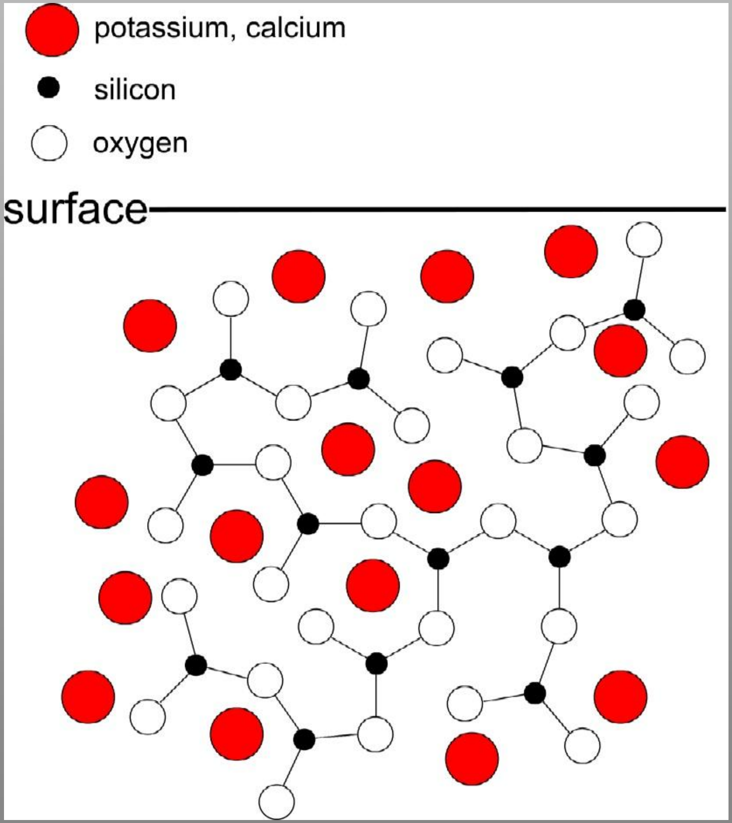


Glass fragments of the Helenistic, Roman and Byzantine Periods



Ancient glass fragments of Ephesos with iridescent surface layers – due to corrosion in moist soil

Theory of Glass Corrosion (I)



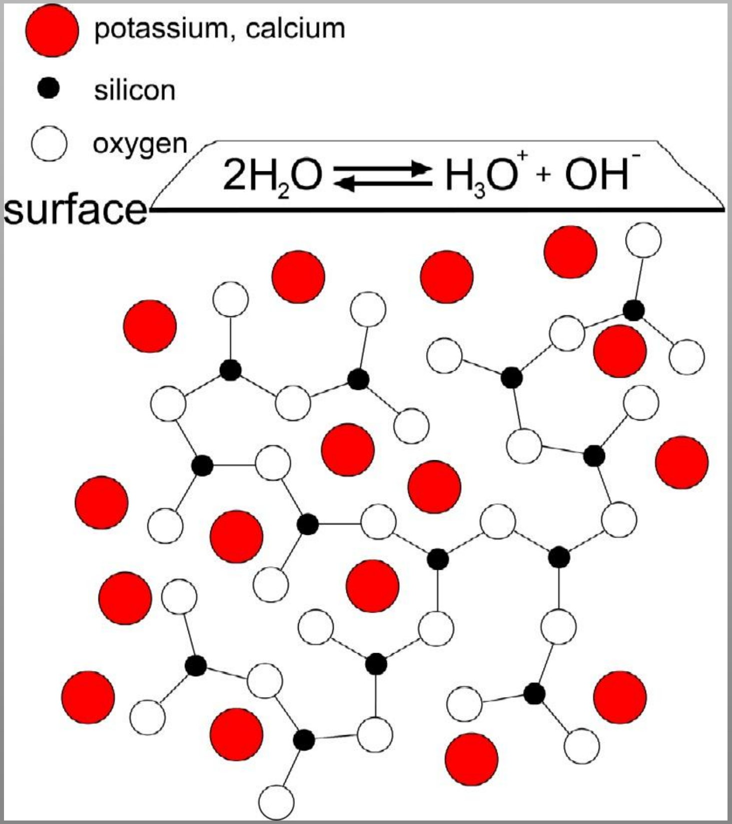
Structure:

⇒ SiO_4-tetrahedra (network former)

⇒ bridging and non-bridging oxygen

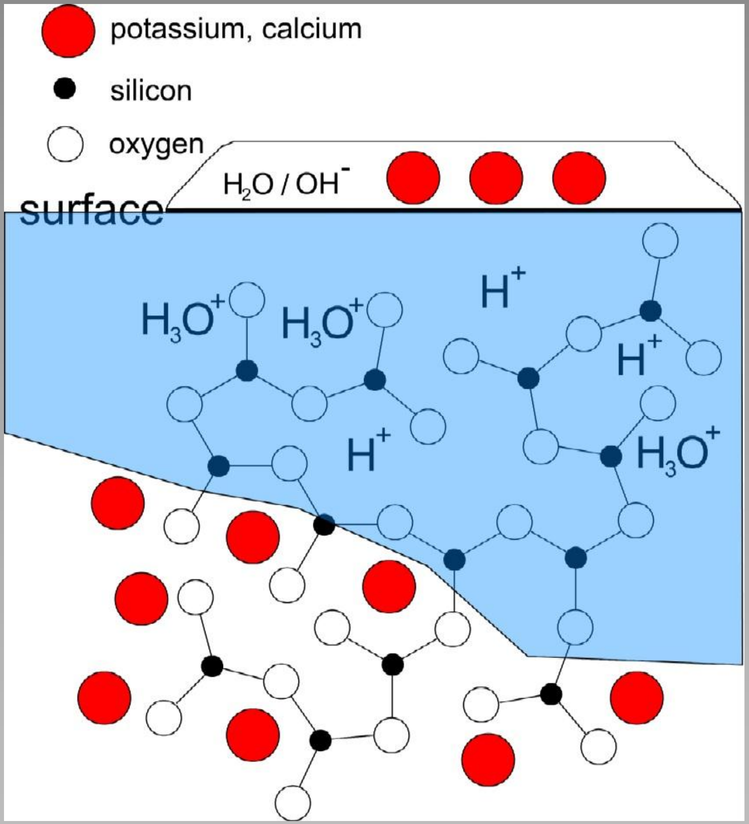
⇒ Na, K, Ca, Mg etc (network modifiers)

Theory of Glass Corrosion (II)



Step 1: formation of a water film

Theory of Glass Corrosion (III)



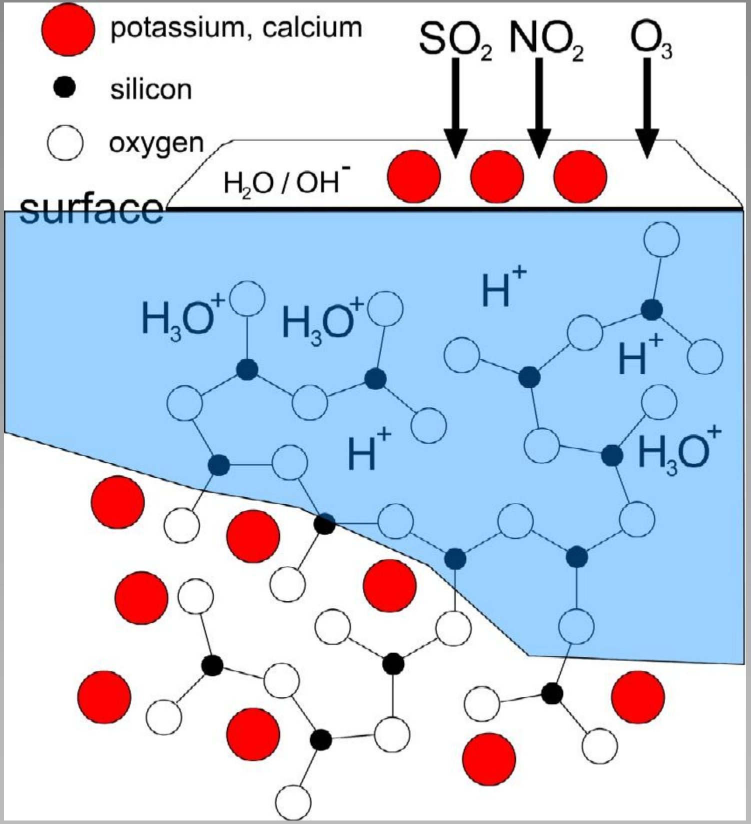
Step 1: formation of a water film

Step 2: ion-exchange H_3O^+/K^+, Ca^{2+}

⇒ formation of a leached layer

optical property of the leached layer is different from the bulk glass
→ **iridescent layer**

Theory of Glass Corrosion (IV) → Weathering



Step 1: formation of a water film

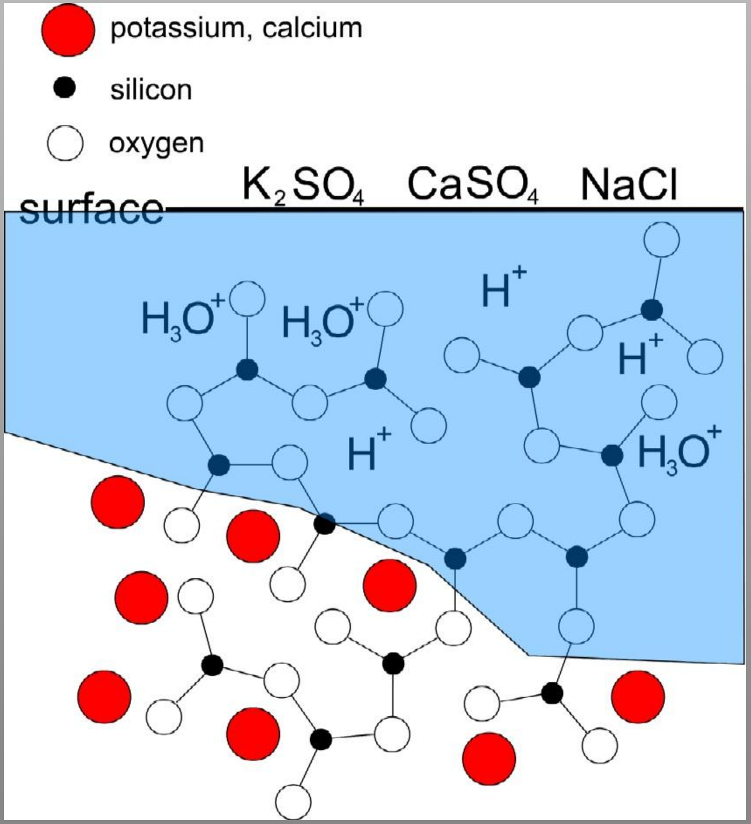
Step 2: ion-exchange H^+/K^+, Ca^{2+}

⇒ formation of a leached layer

Step 3: absorption of acidifying gases

⇒ increase of the amount of H_3O^+

Theory of Glass Corrosion / Weathering (V)



Step 1: formation of a water film

Step 2: ion-exchange H^+/K^+, Ca^{2+}

⇒ formation of a leached layer

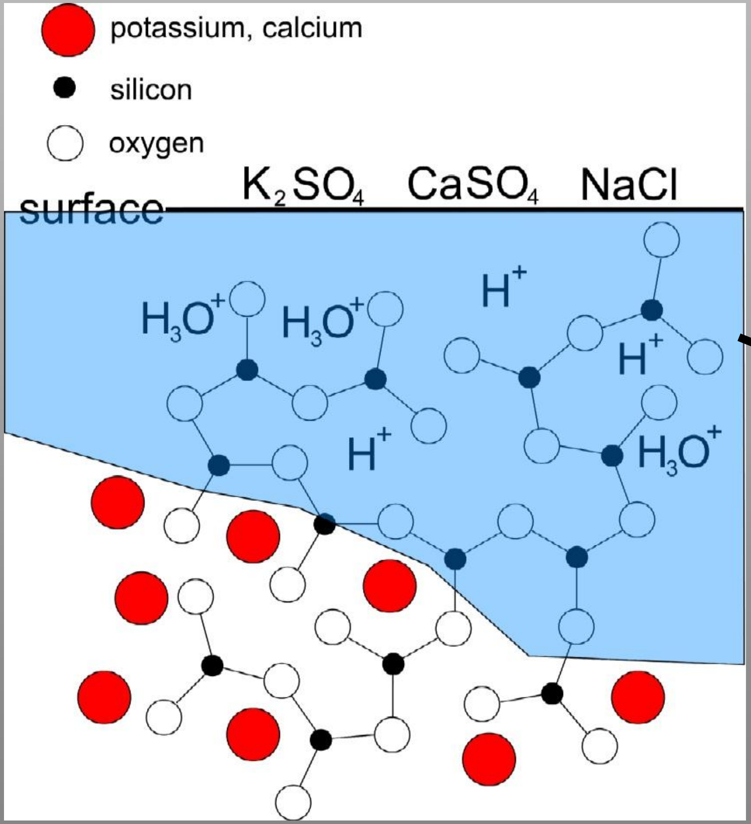
Step 3: absorption of acidifying gases

⇒ increase of the amount of H_3O^+

Step 4: evaporation of water

⇒ formation of precipitates

Theory of Glass Corrosion / Weathering (VI)



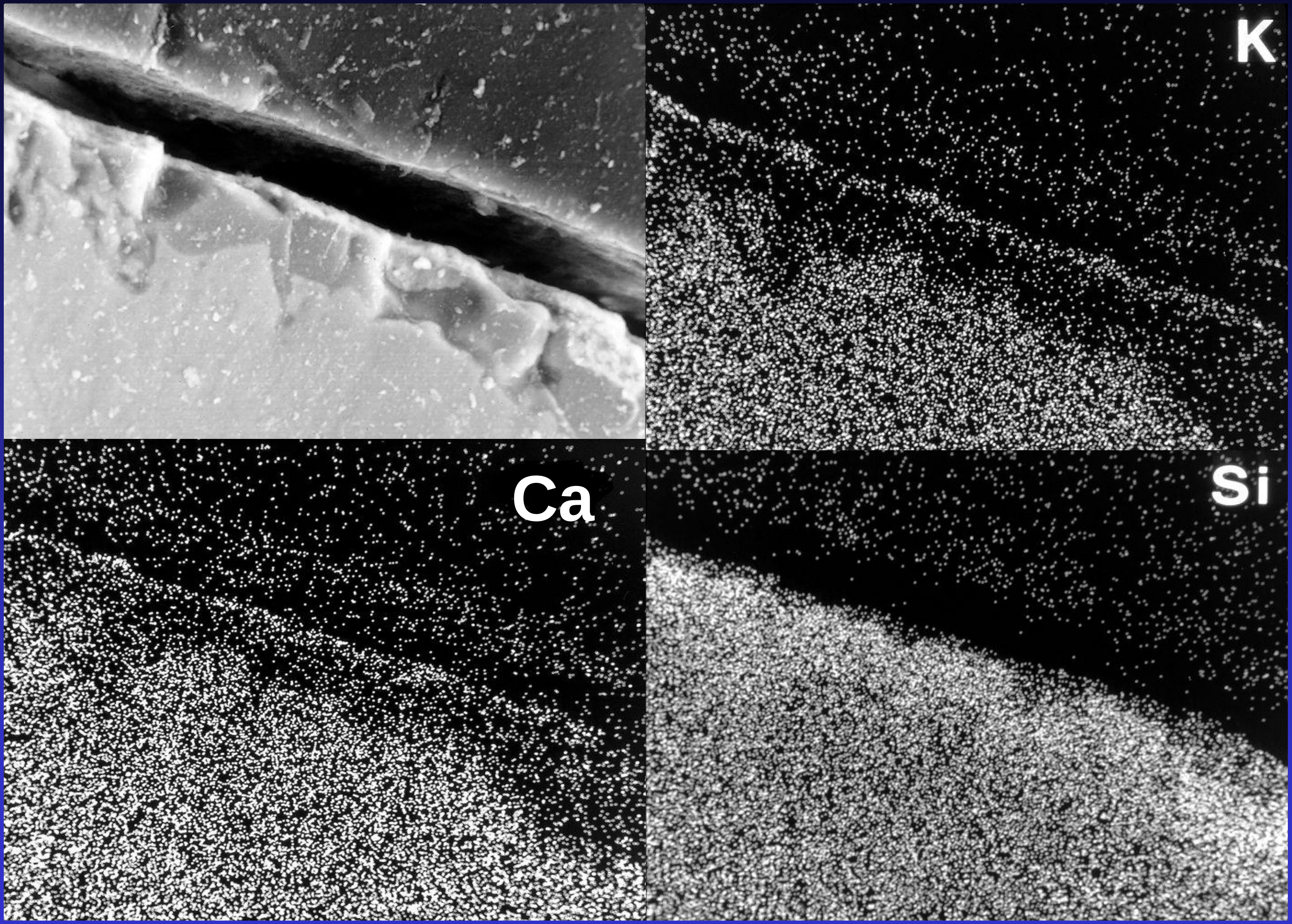
2 effects can be observed

crystals (corrosion products) on the surface

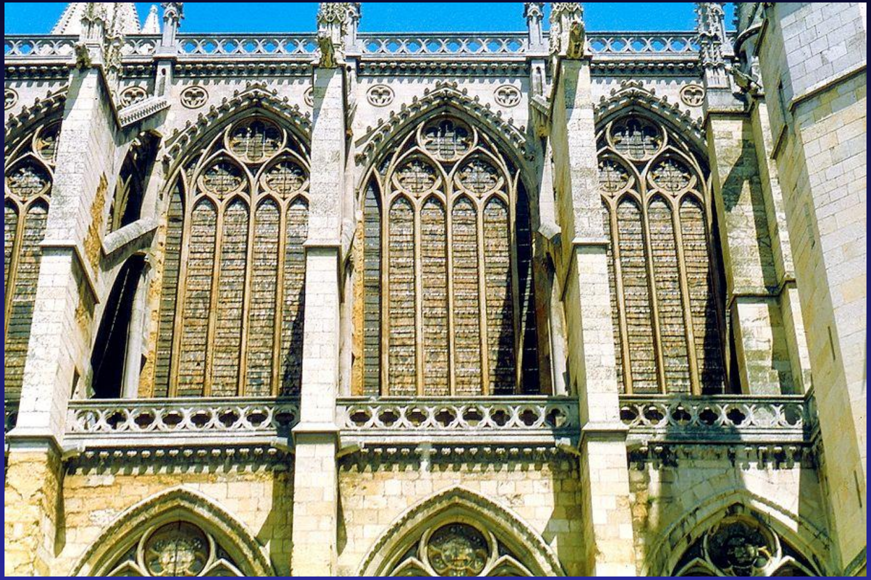
leached layer with depletion of K and Ca and enrichment of hydrogen bearing species

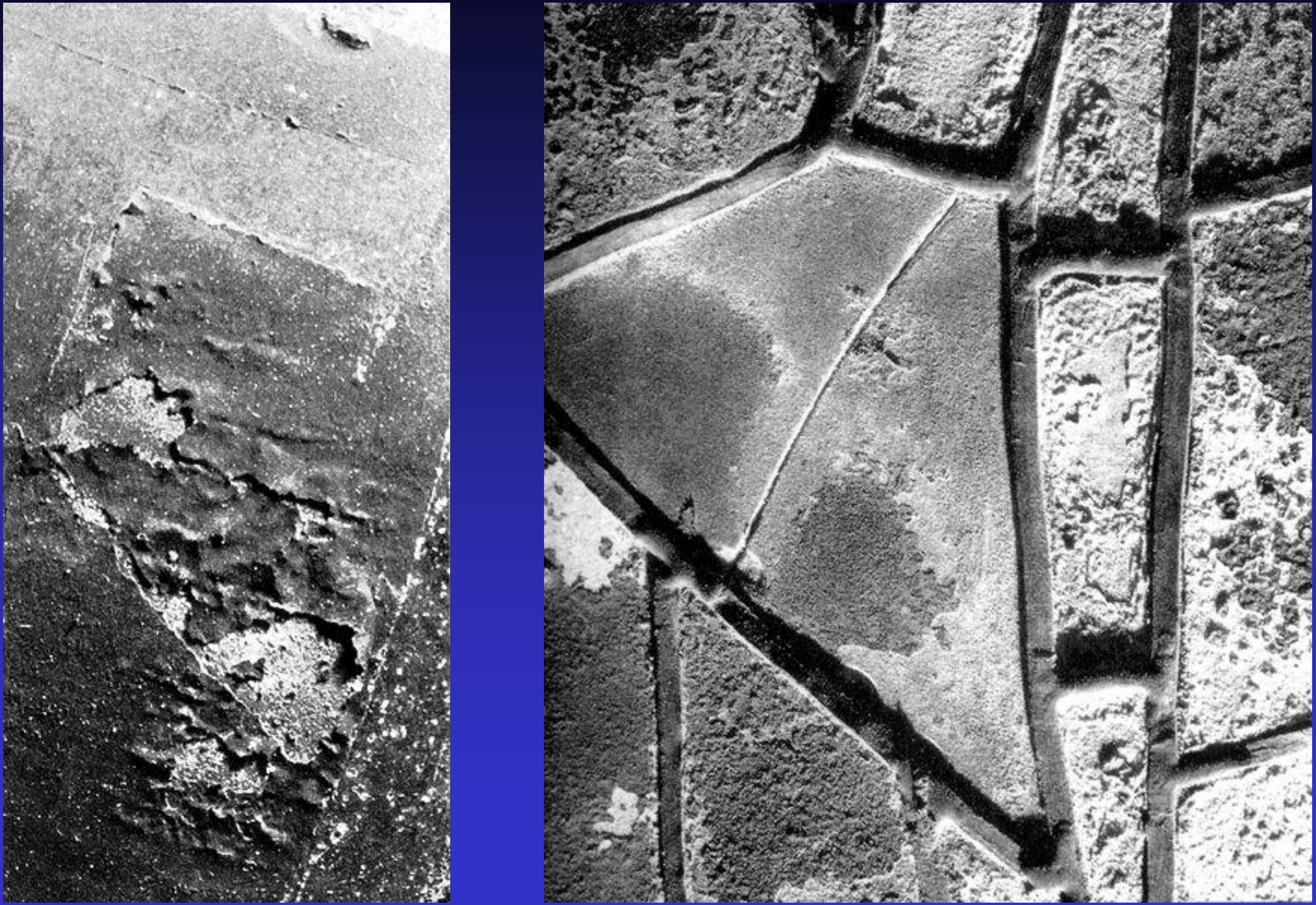
Investigations of the glass degradation:

- XRF / µ-XRF (elemental glass composition, non-destructive)
- SEM/EDS (elemental glass composition)
- SIMS (H content in leached layer)
- µ-Raman (changes in the glass structure)
- XRD (corrosion products)


K
Ca
Si

Medieval Stained Glass (potash glass)

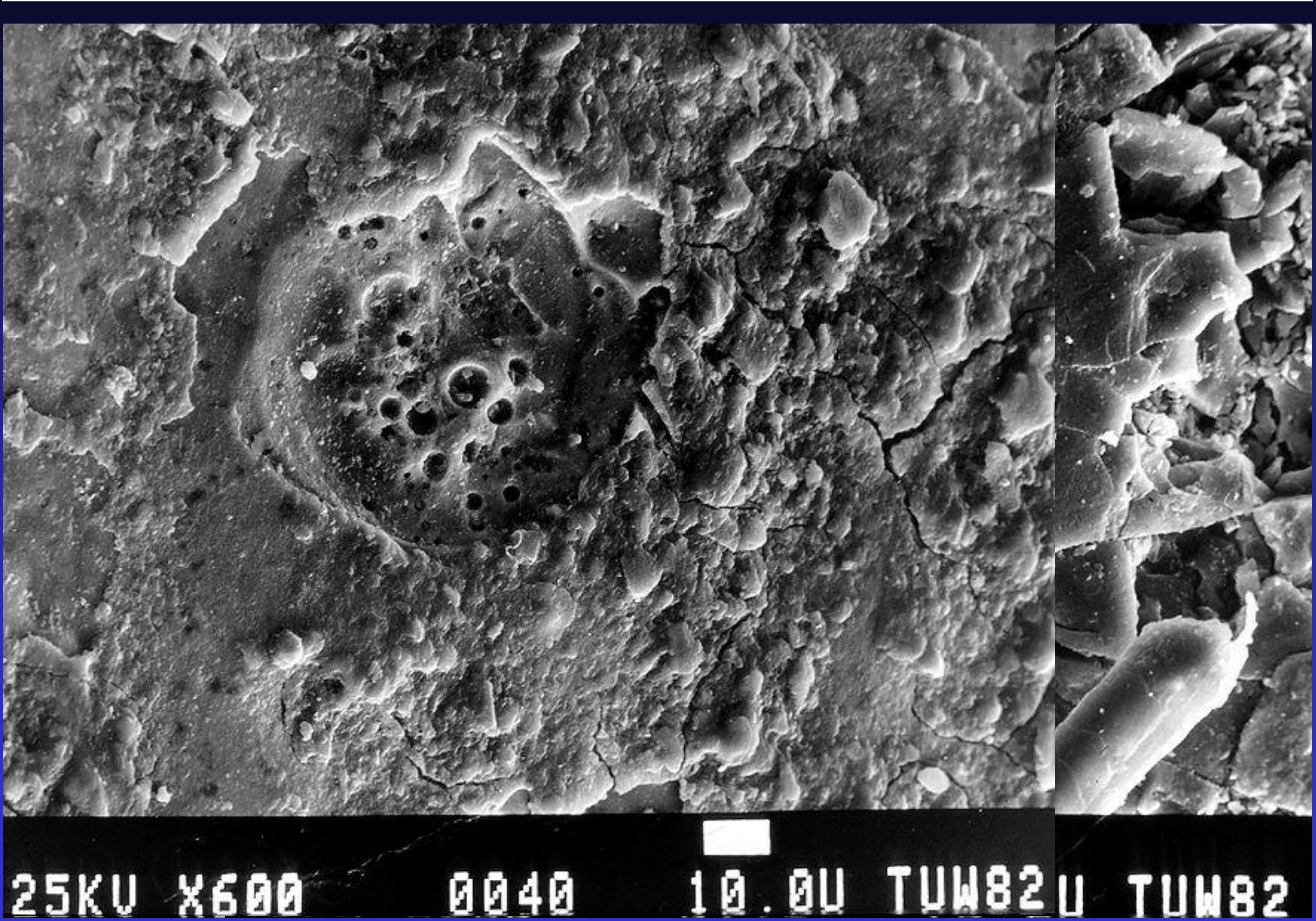




Weathering Crust –

most important corrosion products:

- Syngenite – $K_2SO_4 . CaSO_4 . H_2O$
- Gypsum – $CaSO_4 . 2H_2O$
- Hydrated Silica


25KU X600 0040 10.0U TUW82
U TUW82

Investigations of glass degradation by means of Raman spectroscopy

Case study:

Raman investigation of the structural changes during alteration of historic glasses by organic pollutants
L. Robinet, C. Coupry, K. Eremin and Ch. Hall, J. Raman Spectrosc. **37** (2006) 1278–1286

2 Objects from National Museums of Scotland

- **Soda-silicate glass**
- **Soda-lime-silicate glass**
- **19th to early 20th century**
- **Organic polutants; acetic and formic acid as sources for H^+**

Analysis:

- **532 nm laser**
- **5-9 mW @ the sample**
- **Measurements at cross-sections (intact glass and altered layer)**
- **SEM-EDS (glass composition, at% elements)**
- **SIMS (H- content of the altered region)**

Raman spectra measured between 150 and 1350 cm-1

(vibrations of the silicate structure)

2 main regions:

• 300 – 600 cm-1	bending vibrations within inter-tetrahedral linkages
• 900-1300 cm-1	Si-O stretching vibrations of depolymerised silicate species

Q_n were used to distinguish between different silicate species in the network:

In the examined alkali-silicate glasses:

Only Q_3 (major conc.), Q_2 and Q_4 (both minor conc.) silicate species are present

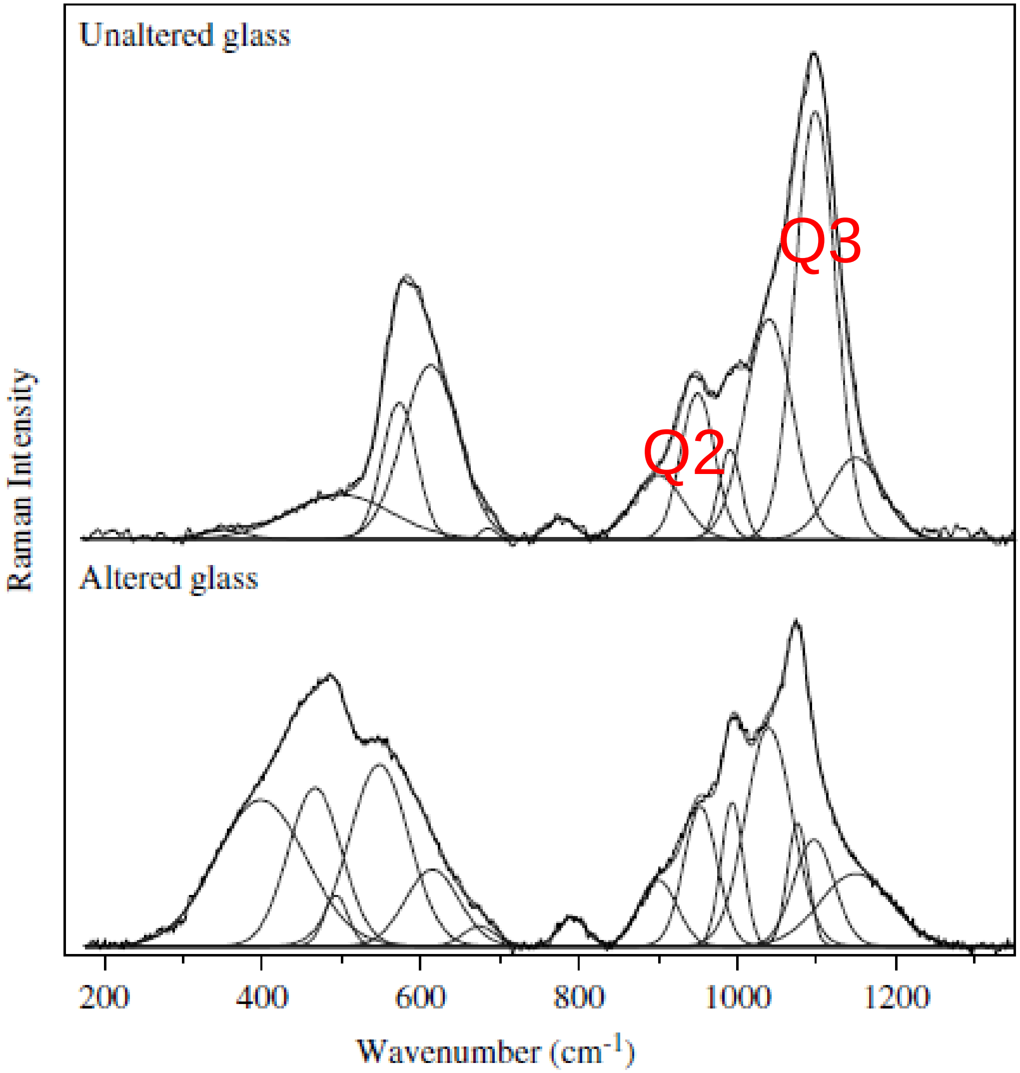


Figure 6. Raman spectra of the altered and unaltered region of the Islamic glass bottle, and their decomposition.

- Decreasing of the 1100 cm^{-1} (Q_3)

  Due to the loss of depolimerised Q_3 species (1 NBO), coordinated : mainly to sodium (Na+)

- Removal of cations

  Shift of the components associeted with Si-O-Si bending in depolym. species from 573 to 548 cm^{-1}

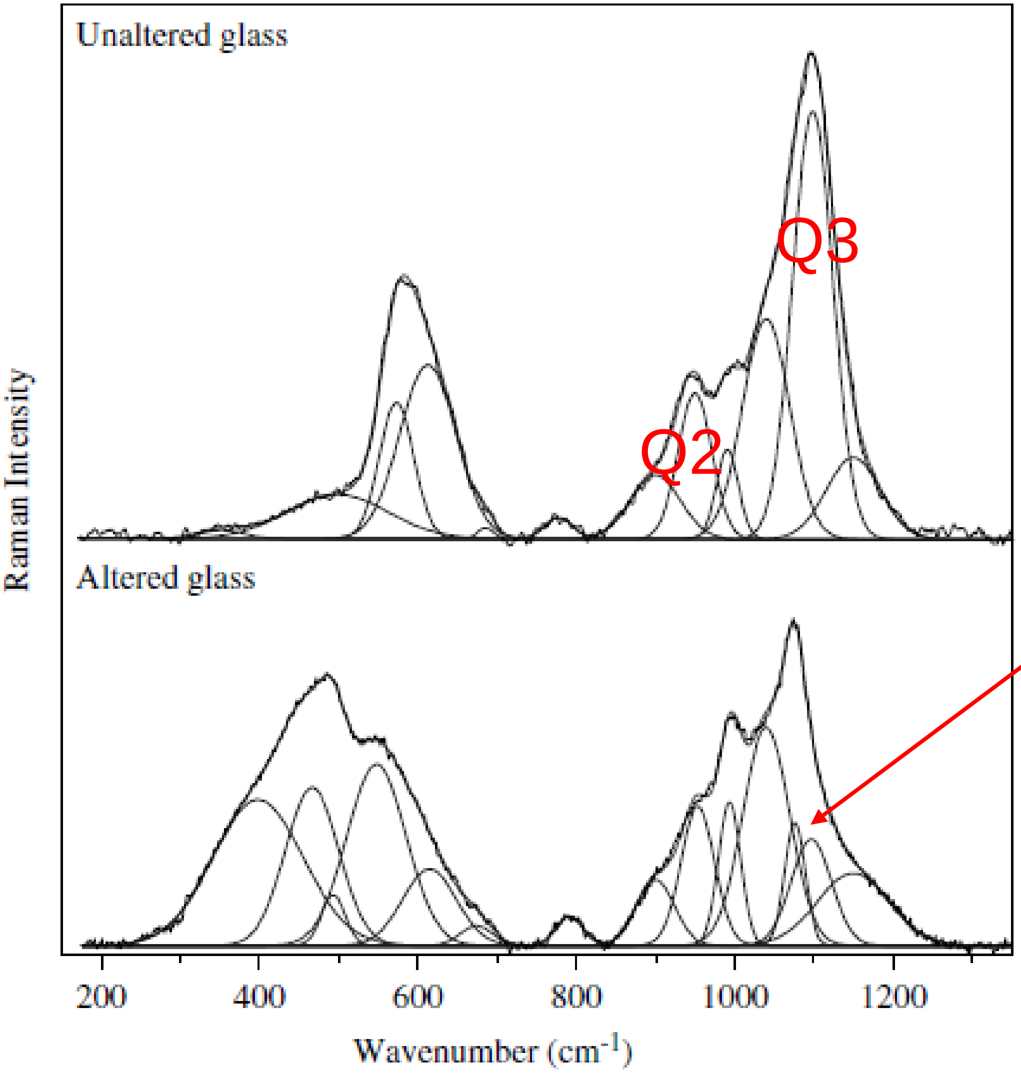


Figure 6. Raman spectra of the altered and unaltered region of the Islamic glass bottle, and their decomposition.

- Q_2 (900-1000 cm^{-1}): stretching, mainly undisturbed, coordinated to Ca^{2+}
- 1075 cm^{-1}: stretching of Si-O bridging bonds: formation of new Si-O-Si linkages

Summary

Raman spectroscopy on glass

- non-destructive
- information about the glass structure
- but: data evaluation is complicated, spectra has to be decomposed in Q_n components
- combination of elemental composition data (electron microprobe) and Raman data makes the work much easier

Acknowledgments

Dr. Michael Melcher

Jelena Djurdjevic

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Introduction to the IRUG Raman spectral database & website software

Gabriel Richards, Ender Technology Corporation, Los Angeles, US

Beth Price, Andrew Lins, Philadelphia Museum of Art, US

Boris Pretzel, Victoria and Albert Museum, London, UK

Charles Davis, The Dow Chemical Company, Philadelphia, US

Suzanne Lomax, National Gallery of Art, US

Marcello Picollo, IFAC-CNR

THURSDAY, SEPTEMBER 27: LECTURE 8

Introduction to the IRUG Raman Spectral Database and Website

Beth A. Price, Andrew Lins, Philadelphia Museum of Art

Charles Davis, The Dow Chemical Company

Boris Pretzel, Victoria and Albert Museum

Gabriel Richards, Steve Rice, Endertech

Suzanne Quillen Lomax, National Gallery of Art

Marcello Picollo, IFAC-CNR

IRUG Raman
Spectroscopy Workshop
Philadelphia Museum of Art
27 – 28 September 2012

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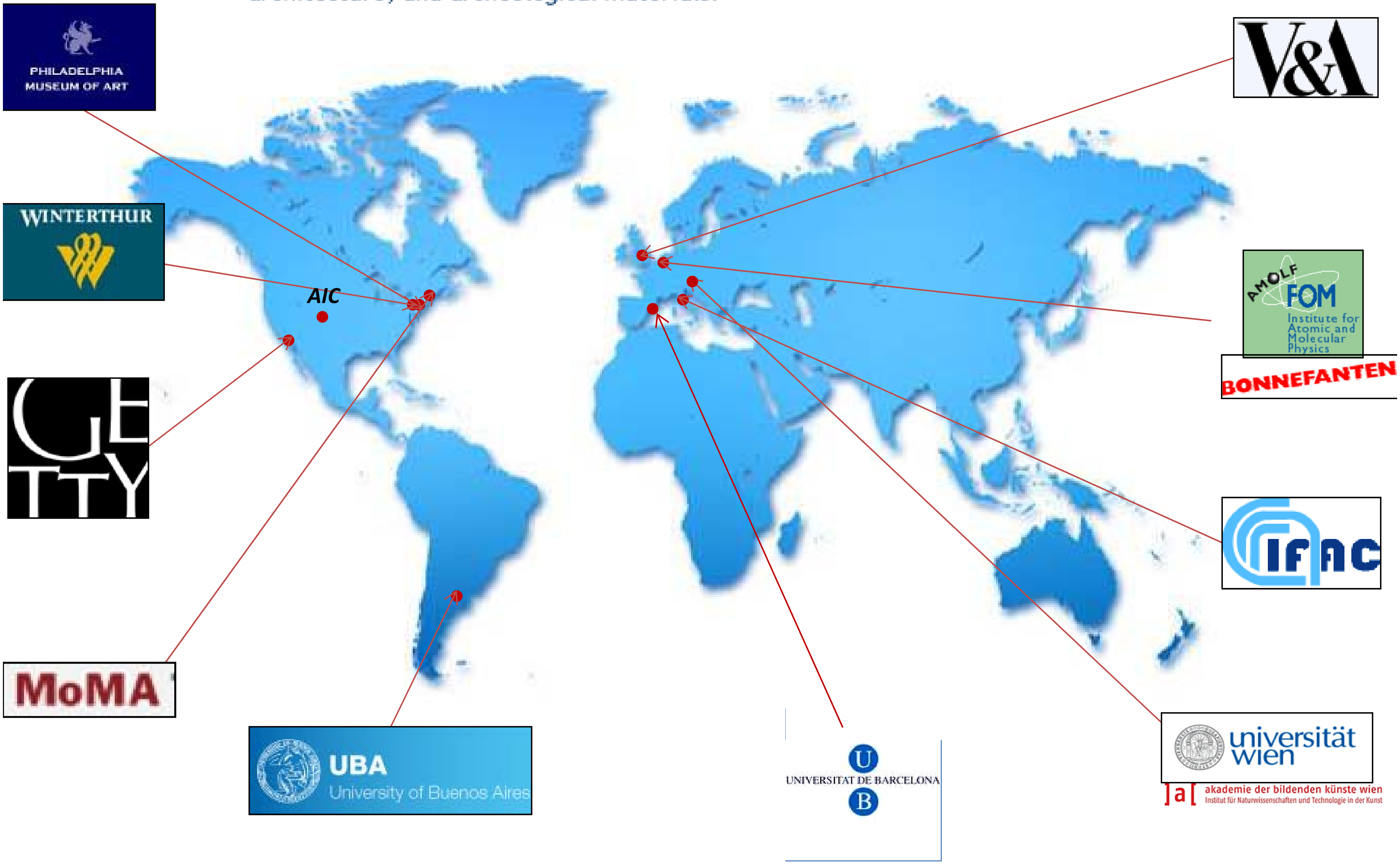
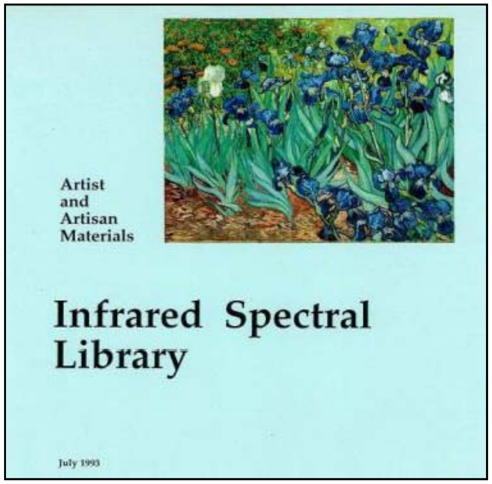


IR Databases 1993-2009

1993

777 spectra
9 institutions



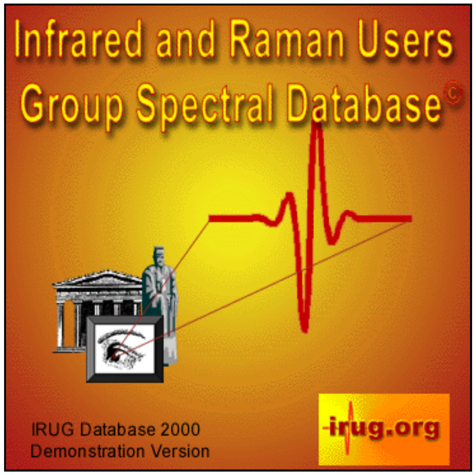
Artist
and
Artisan
Materials

Infrared Spectral
Library

July 1993

2002

1254 spectra
100 institutions



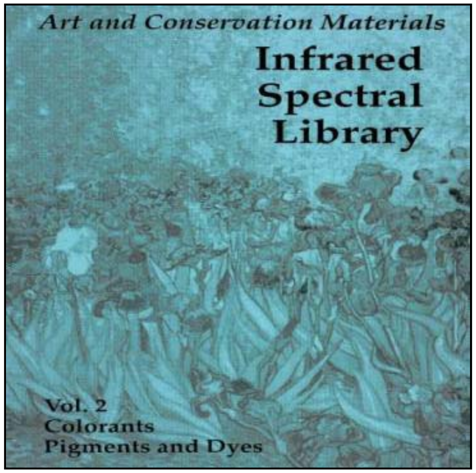
Infrared and Raman Users
Group Spectral Database©

IRUG Database 2000
Demonstration Version

irug.org

1994-5

1259 spectra
21 institutions



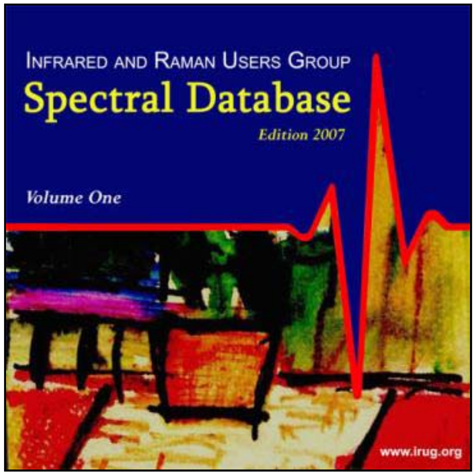
Art and Conservation Materials

Infrared
Spectral
Library

Vol. 2
Colorants
Pigments and Dyes

2009

2,128 spectra
100+ institutions

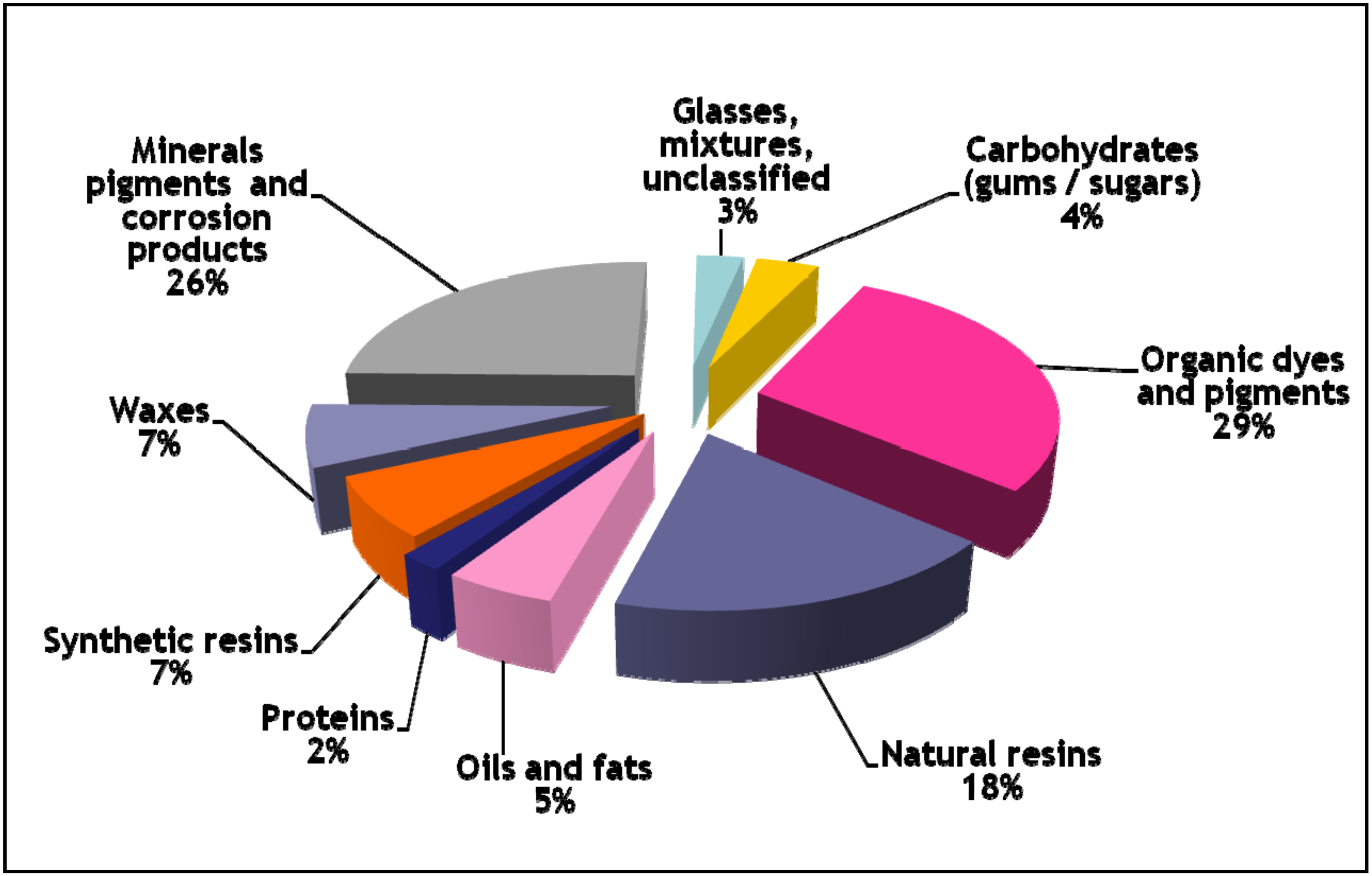


INFRARED AND RAMAN USERS GROUP
Spectral Database
Edition 2007

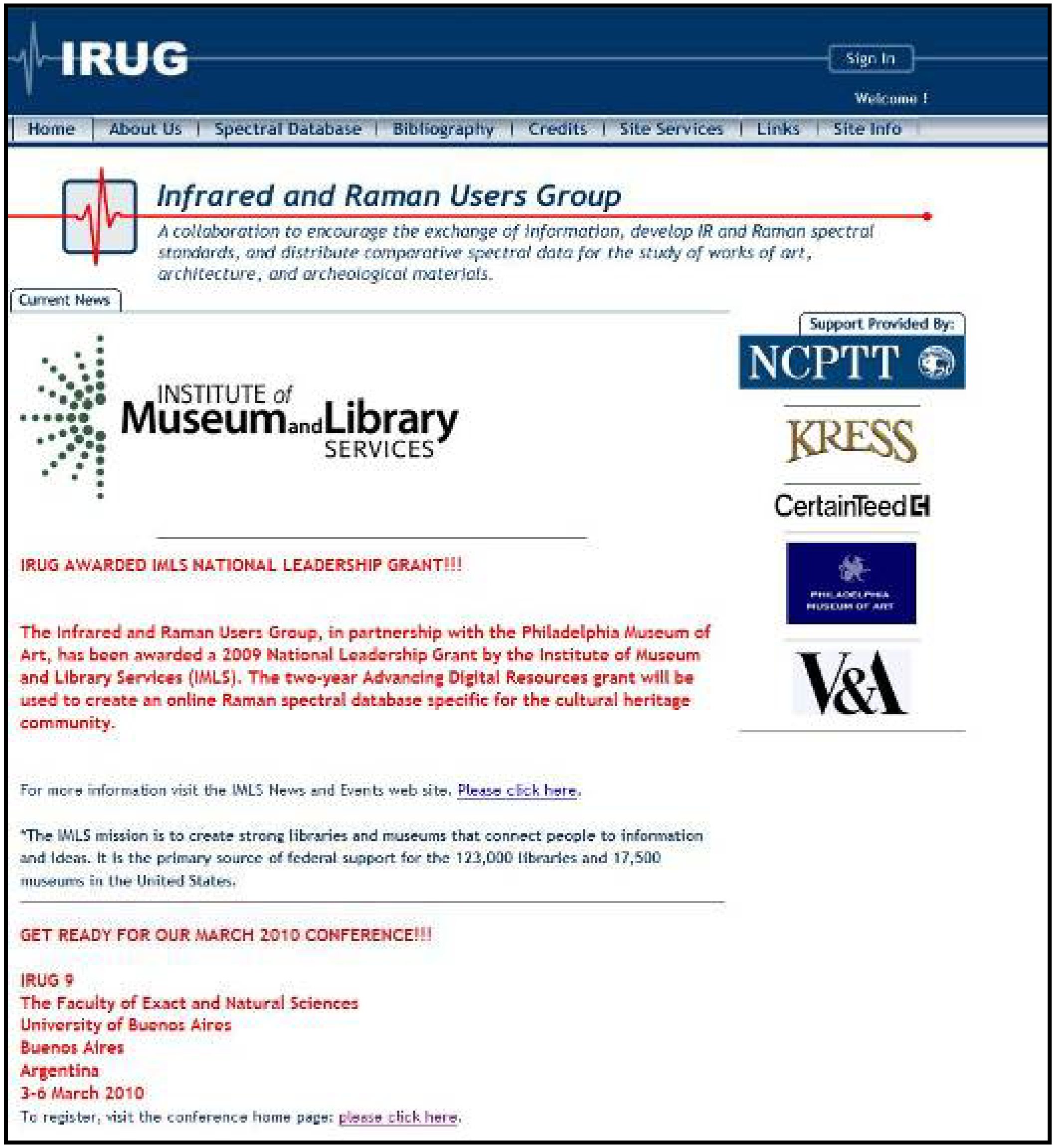
Volume One

www.irug.org

Database Composition (IR)



IRUG Website



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The Infrared and Raman Users Group, in partnership with the Philadelphia Museum of Art, has been awarded a 2009 National Leadership Grant by the Institute of Museum and Library Services (IMLS). The two-year Advancing Digital Resources grant will be used to create an online Raman spectral database specific for the cultural heritage community.

For more information visit the IMLS News and Events web site. Please click here.

*The IMLS mission is to create strong libraries and museums that connect people to information and Ideas. It is the primary source of federal support for the 123,000 libraries and 17,500 museums in the United States.

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IRUG 9
The Faculty of Exact and Natural Sciences
University of Buenos Aires
Buenos Aires
Argentina
3-6 March 2010
To register, visit the conference home page: please click here.

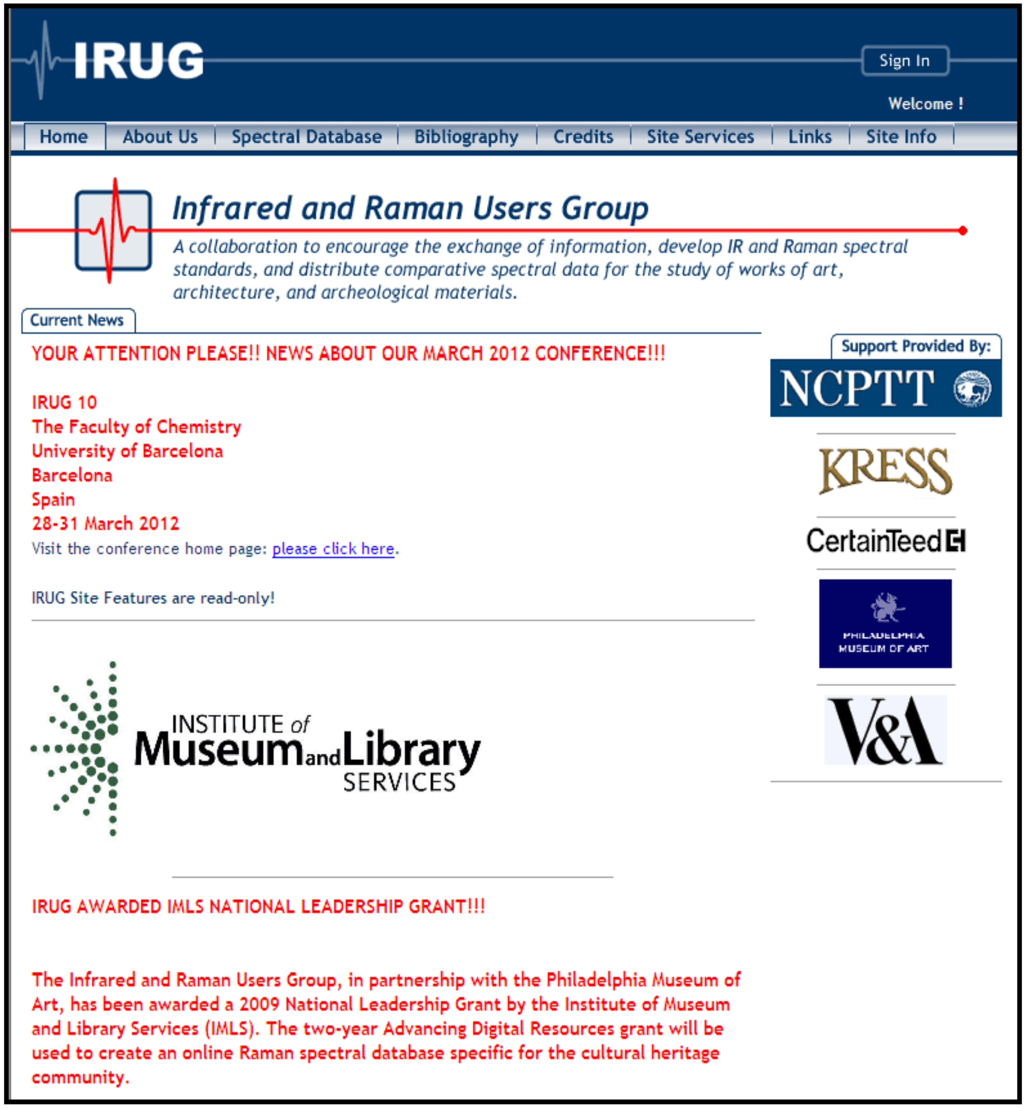
1999

- **www.irug.org** launched

2002

- **NCPTT grant**
- Website software to submit, review, store, distribute spectra

IRUG Website: www.irug.org



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IRUG 10
The Faculty of Chemistry
University of Barcelona
Barcelona
Spain
28-31 March 2012
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IRUG Site Features are read-only!

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2002

- **NCPTT grant**
- Website software to submit, review, store, distribute spectra

Swwubmit spectra

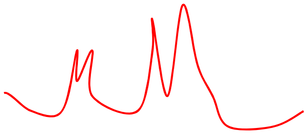
Track: review progress

Receive: returned spectra with editorial comment

Download: IRUG spectral database and periodic updates

Future features: search unknowns on-line against database manipulate spectra etc

Contributor



Search and print out: **IRUG** spectra (by name)

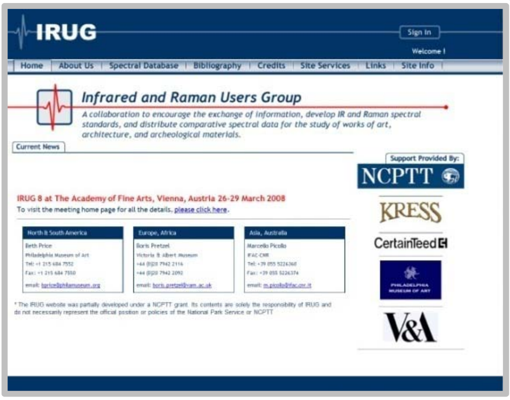
Search: IRUG citations

Participate: in IRUG on-line discussion forum

Keep abreast: of new IRUG initiatives

Future features: (limited) search unknowns against IRUG database

User



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IRUG 8 at The Academy of Fine Arts, Vienna, Austria 26-29 March 2008

To visit the meeting home page for all the details, please click here.

North & South America	Europe, Africa	Asia, Australia
Beth Price Philadelphia Museum of Art Tel: +1 215 684 7552 Fax: +1 215 684 7550 email: bprice@philamuseum.org	Boris Pretzel Victoria & Albert Museum +44 (0)20 7942 2116 +44 (0)20 7942 2092 email: boris.pretzel@vam.ac.uk	Marcello Picollo IFAC-CNR Tel: +39 055 5226360 Fax: +39 055 5226374 email: m.picollo@ifac.cnr.it

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IRUG website, **www.irug.org**

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Review and quality assure submissions

Receive: submissions in allocated materials classes

Submit: new entries for citations

Participate: in reviewers discussion forum

Senior editor

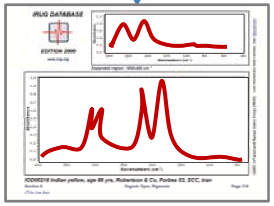
Receive: new submissions

Receive: comments and reviews from reviewers

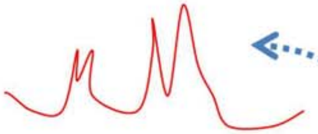
Manipulate and adjust: submitted spectra

Vote: keep or return submission

Participate: in senior editors' discussion forum



IRUG spectral database



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- **Search** on-line bibliography
- **Participate** in on-line discussion forum
- **Keep abreast** of IRUG initiatives

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- **Track** review progress
- **Receive** returned spectra with editorial comments
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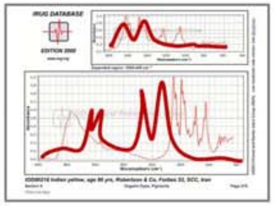


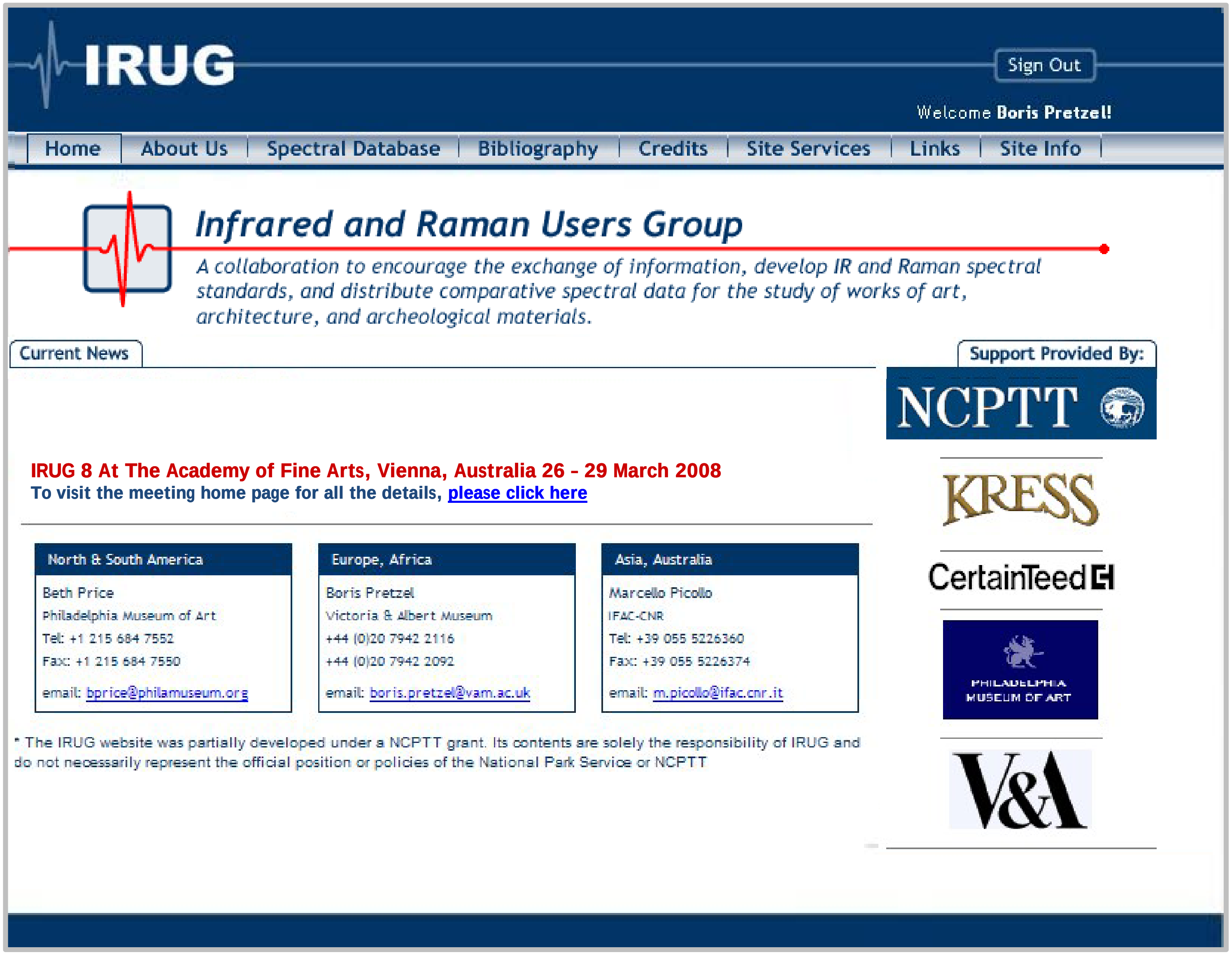
IRUG spectral database

Reviewer:

- **Review** and quality assure submissions
- **Receive** new submission in selected materials classes
- **Submit** new entries for citations
- **Participate** in reviewers discussion forum

Senior editor:

- **Receive** new submissions
- **Receive** comments and reviews from reviewers
- **Manipulate** and adjust submitted spectra
- **Participate** in senior editors discussion forum



Welcome **Boris Pretzel!**

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IRUG 8 At The Academy of Fine Arts, Vienna, Australia 26 - 29 March 2008

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Philadelphia Museum of Art	Victoria & Albert Museum	IFAC-CNR
Tel: +1 215 684 7552	+44 (0)20 7942 2116	Tel: +39 055 5226360
Fax: +1 215 684 7550	+44 (0)20 7942 2092	Fax: +39 055 5226374
email: bprice@philamuseum.org	email: boris.pretzel@vam.ac.uk	email: m.picollo@ifac.cnr.it

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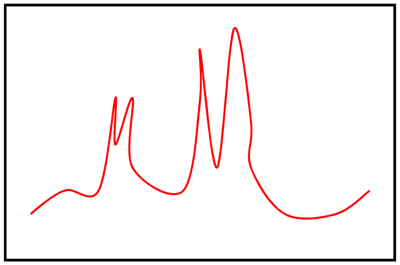

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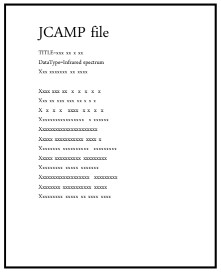

JCAMP file

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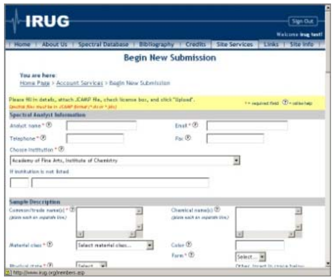

Begin New Submission

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Home Page > Account Services > Begin New Submission

Please fill in details, attach JCAMP file, check license box, and click "Upload".

Spectral Analyst Information

Analyst name *
Email *
Telephone *
Fax
Choose Institution *
Academy of Fine Arts, Institute of Chemistry
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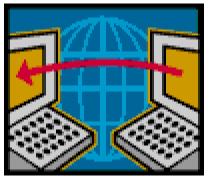
Sample Description

Common/trade name(s) *
Chemical name(s)
Material class * Select material class...
Color
Form * Select...

Add supporting information



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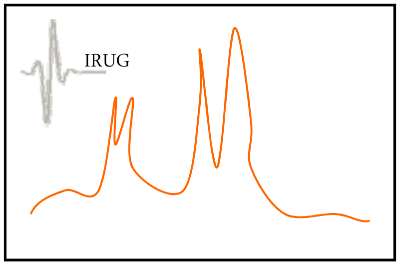

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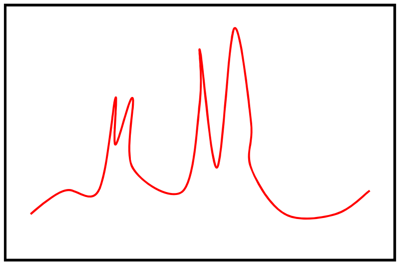
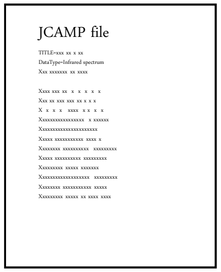
Spectrum in
absorbance



Convert to
JCAMP-dx



JCAMP file

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Xxxx xxx xx x x x x x
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X x x x xxxx x x x x
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Xxxxxxxxxxxxxxxxxxxxx
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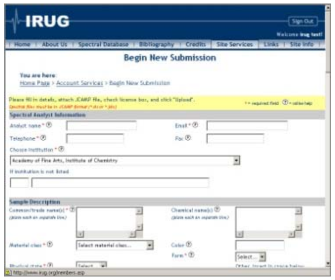
www.irug.org
and upload



Welcome irug test!

Begin New Submission

You are here:
Home Page > Account Services > Begin New Submission

Please fill in details, attach JCAMP file, check license box, and click "Upload".
Spectral files must be in JCAMP format (*.dx or *.jdx)

Spectral Analyst Information

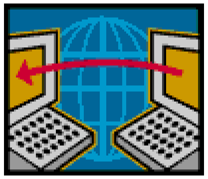
Analyst name *
Email *
Telephone *
Fax
Choose Institution *
Academy of Fine Arts, Institute of Chemistry
If institution is not listed

Sample Description

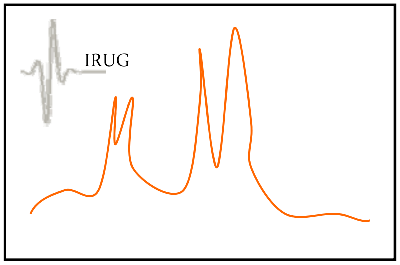
Common/trade name(s) * (place each on separate line)
Chemical name(s) (place each on separate line)
Material class * Select material class...
Color
Form * Select...

http://www.irug.org/members.asp

Add supporting
information

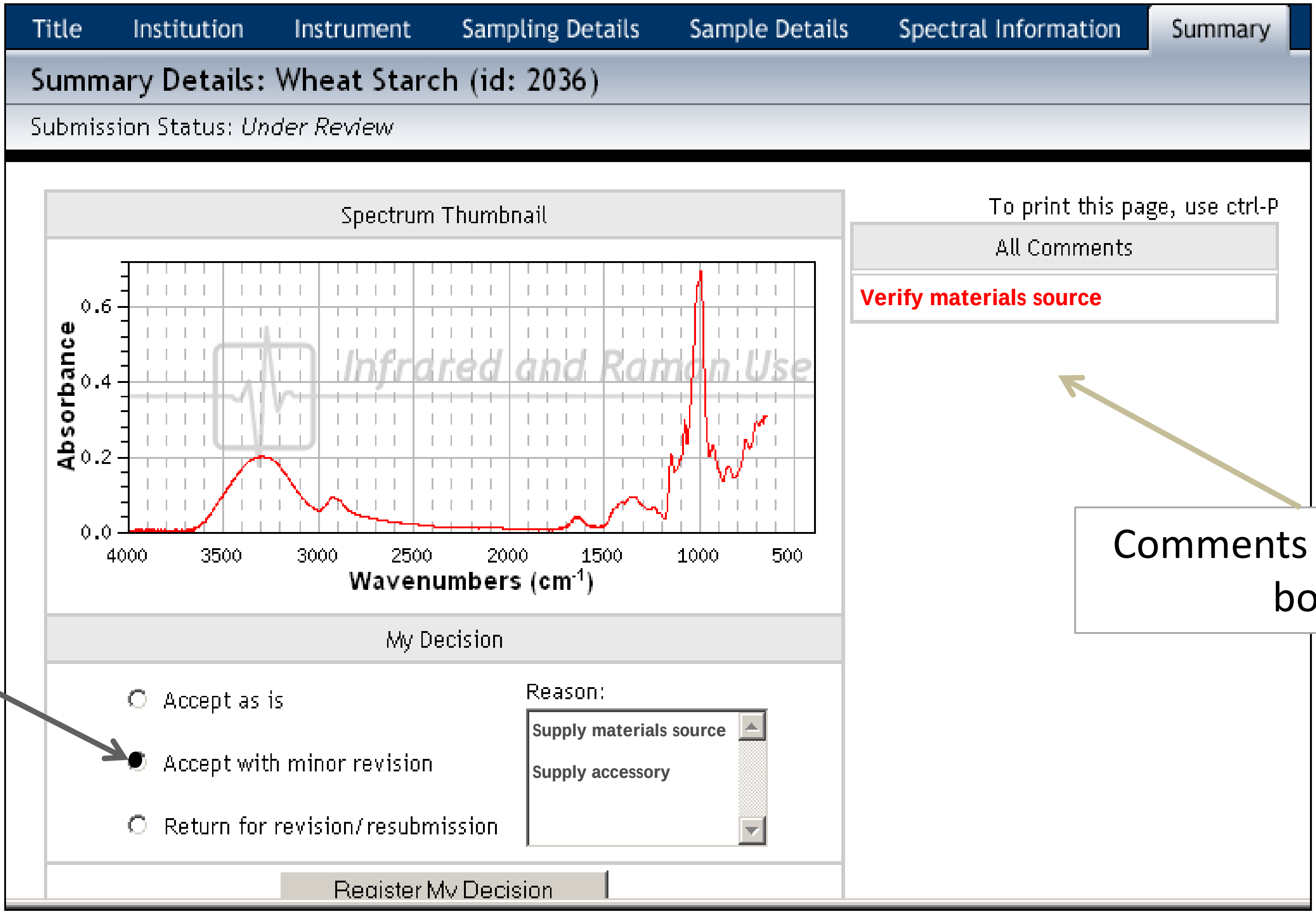


Submit for review
and evaluation



IRUG incorporated
digital file

Editors Tool



Summary Details: Wheat Starch (id: 2036)

Submission Status: *Under Review*

To print this page, use ctrl-P

Verify materials source

○ Accept as is

● Accept with minor revision

○ Return for revision/resubmission

Reason:

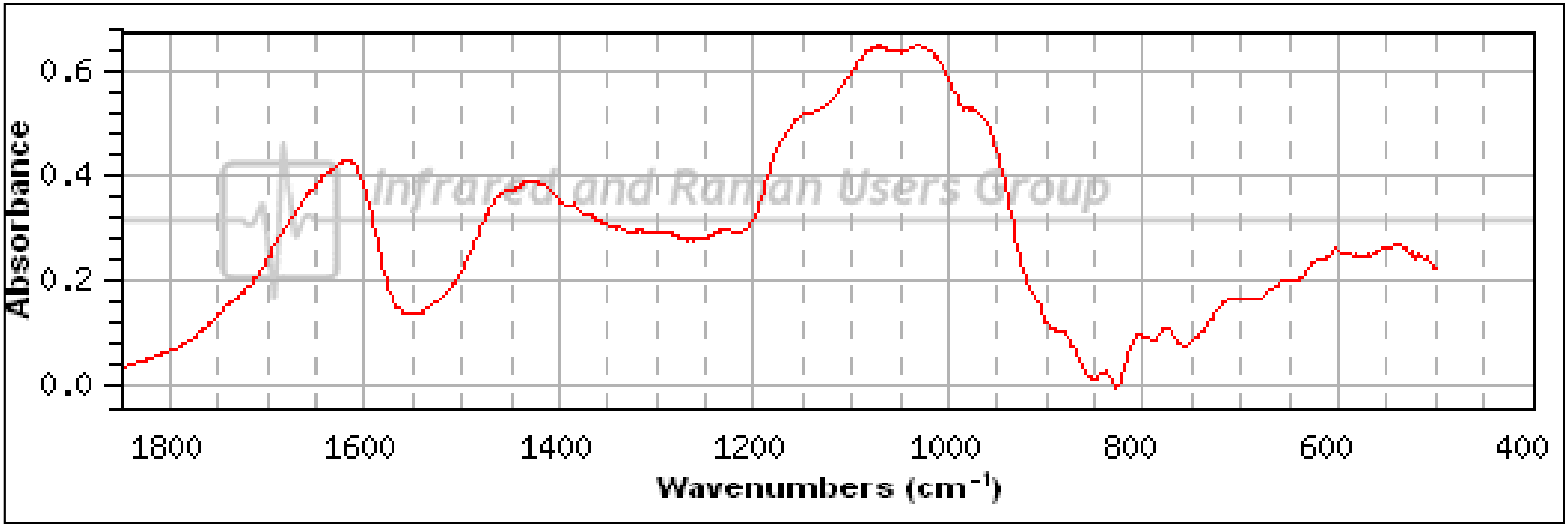
Supply materials source

Supply accessory

Voting options

Comments summary box

2,128 Spectra & Counting



All digitized, peer-reviewed, IRUG-JCAMP.DX formatted spectra from 100+ institutions

North & South America

Beth Price
Philadelphia Museum of Art
Tel: +1 215 684 7552
Fax: +1 215 684 7550

email: bprice@philamuseum.org

Europe, Africa

Boris Pretzel
Victoria & Albert Museum
+44 (0)20 7942 2116
+44 (0)20 7942 2092

email: boris.pretzel@vam.ac.uk

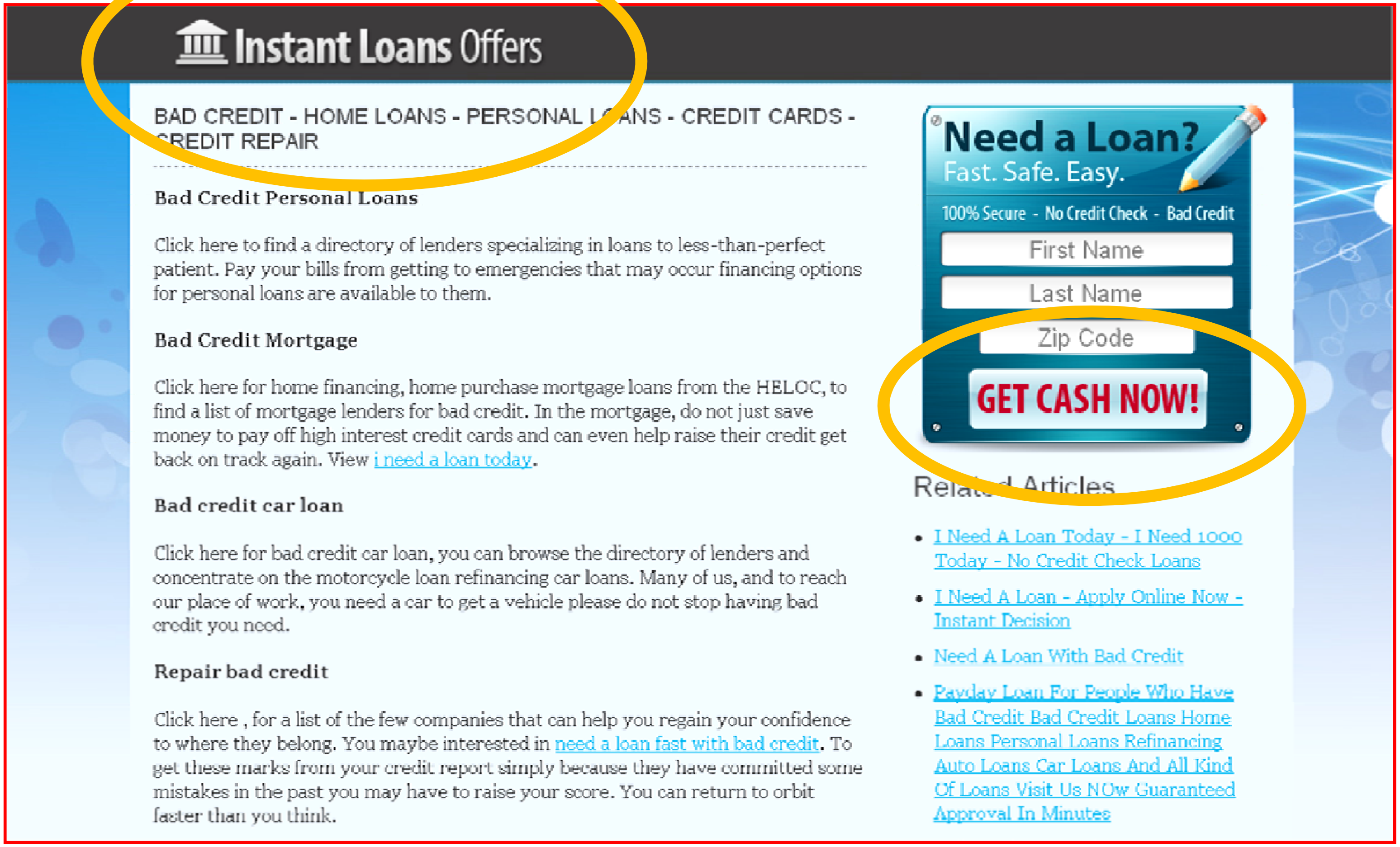
Asia, Australia

Marcello Picollo
IFAC-CNR
Tel: +39 055 5226360
Fax: +39 055 5226374

email: m.picollo@ifac.cnr.it

IRUG

Security issues



BAD CREDIT - HOME LOANS - PERSONAL LOANS - CREDIT CARDS - CREDIT REPAIR

Bad Credit Personal Loans

Click here to find a directory of lenders specializing in loans to less-than-perfect patient. Pay your bills from getting to emergencies that may occur financing options for personal loans are available to them.

Bad Credit Mortgage

Click here for home financing, home purchase mortgage loans from the HELOC, to find a list of mortgage lenders for bad credit. In the mortgage, do not just save money to pay off high interest credit cards and can even help raise their credit get back on track again. View i need a loan today.

Bad credit car loan

Click here for bad credit car loan, you can browse the directory of lenders and concentrate on the motorcycle loan refinancing car loans. Many of us, and to reach our place of work, you need a car to get a vehicle please do not stop having bad credit you need.

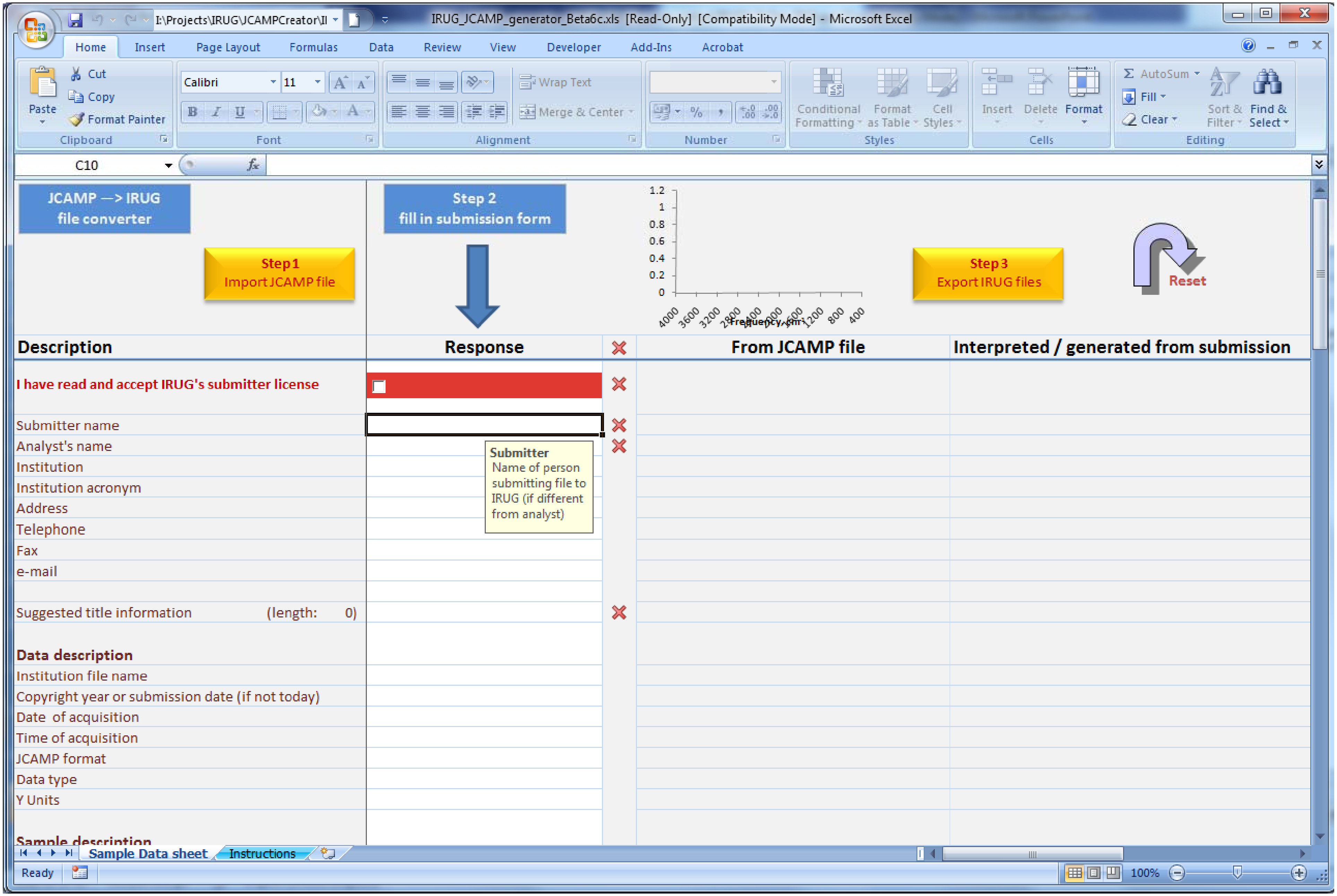
Repair bad credit

Click here , for a list of the few companies that can help you regain your confidence to where they belong. You maybe interested in need a loan fast with bad credit. To get these marks from your credit report simply because they have committed some mistakes in the past you may have to raise your score. You can return to orbit faster than you think.

Related Articles

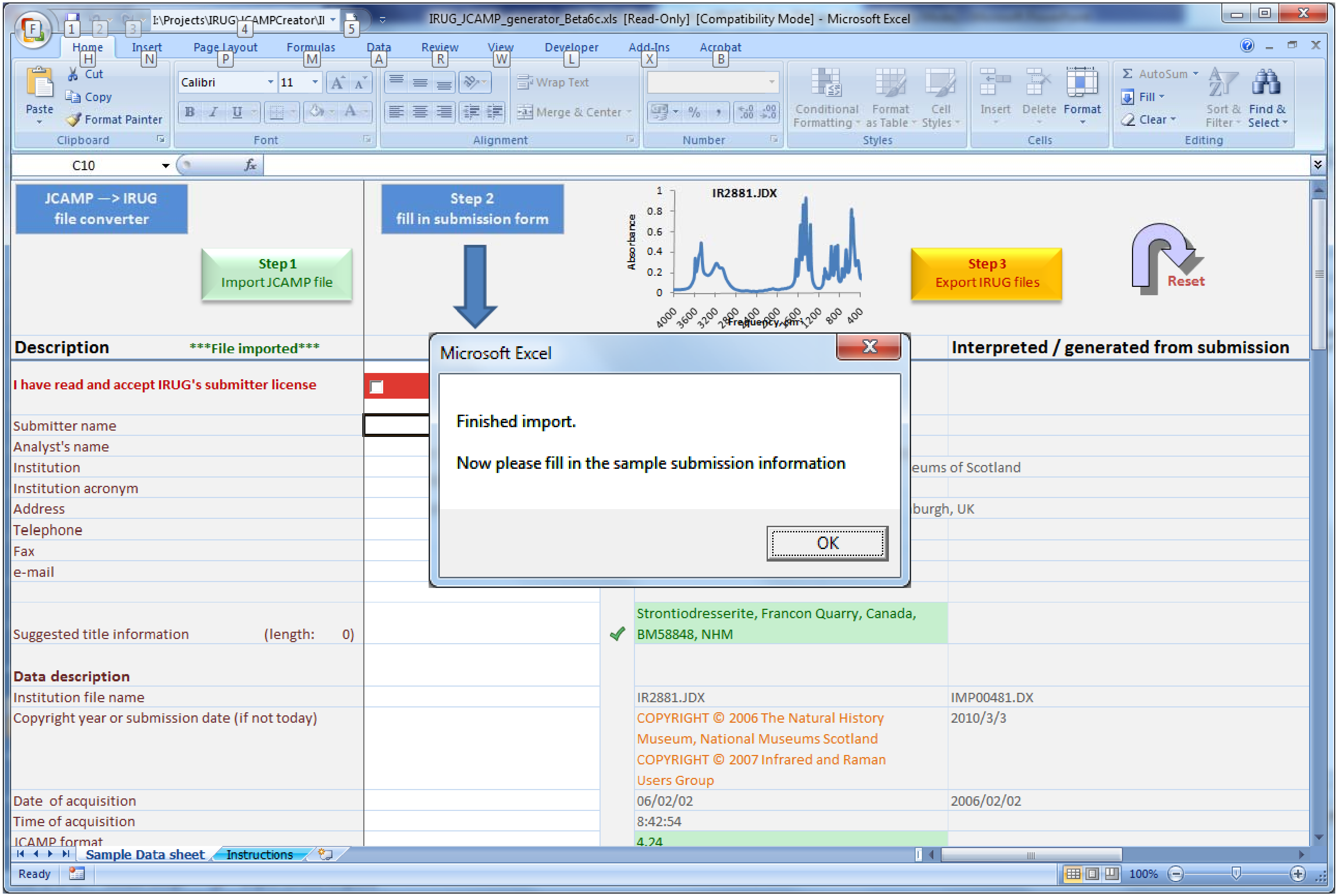
- I Need A Loan Today - I Need 1000 Today - No Credit Check Loans
- I Need A Loan - Apply Online Now - Instant Decision
- Need A Loan With Bad Credit
- Payday Loan For People Who Have Bad Credit Bad Credit Loans Home Loans Personal Loans Refinancing Auto Loans Car Loans And All Kind Of Loans Visit Us NOw Guaranteed Approval In Minutes

SQL server injection viruses create data-corrupting commands & insert hyperlinks to sites like this one. Old IRUG programming vulnerable.



Description	Response	✗	From JCAMP file	Interpreted / generated from submission
I have read and accept IRUG's submitter license	☐	✗		
Submitter name		✗		
Analyst's name		✗		
Institution				
Institution acronym				
Address				
Telephone				
Fax				
e-mail				
Suggested title information (length: 0)		✗		
Data description				
Institution file name				
Copyright year or submission date (if not today)				
Date of acquisition				
Time of acquisition				
JCAMP format				
Data type				
Y Units				
Sample description				

Submitter
Name of person submitting file to IRUG (if different from analyst)



Description ***File imported***

Interpreted / generated from submission

I have read and accept IRUG's submitter license ☐

Submitter name
Analyst's name
Institution ...eums of Scotland
Institution acronym
Address ...burgh, UK
Telephone
Fax
e-mail

Suggested title information (length: 0) ✓ Strontiodresserite, Francon Quarry, Canada, BM58848, NHM

Data description

Institution file name IR2881.JDX IMP00481.DX

Copyright year or submission date (if not today) COPYRIGHT © 2006 The Natural History Museum, National Museums Scotland COPYRIGHT © 2007 Infrared and Raman Users Group 2010/3/3

Date of acquisition 06/02/02 2006/02/02

Time of acquisition 8:42:54

JCAMP format 4.24

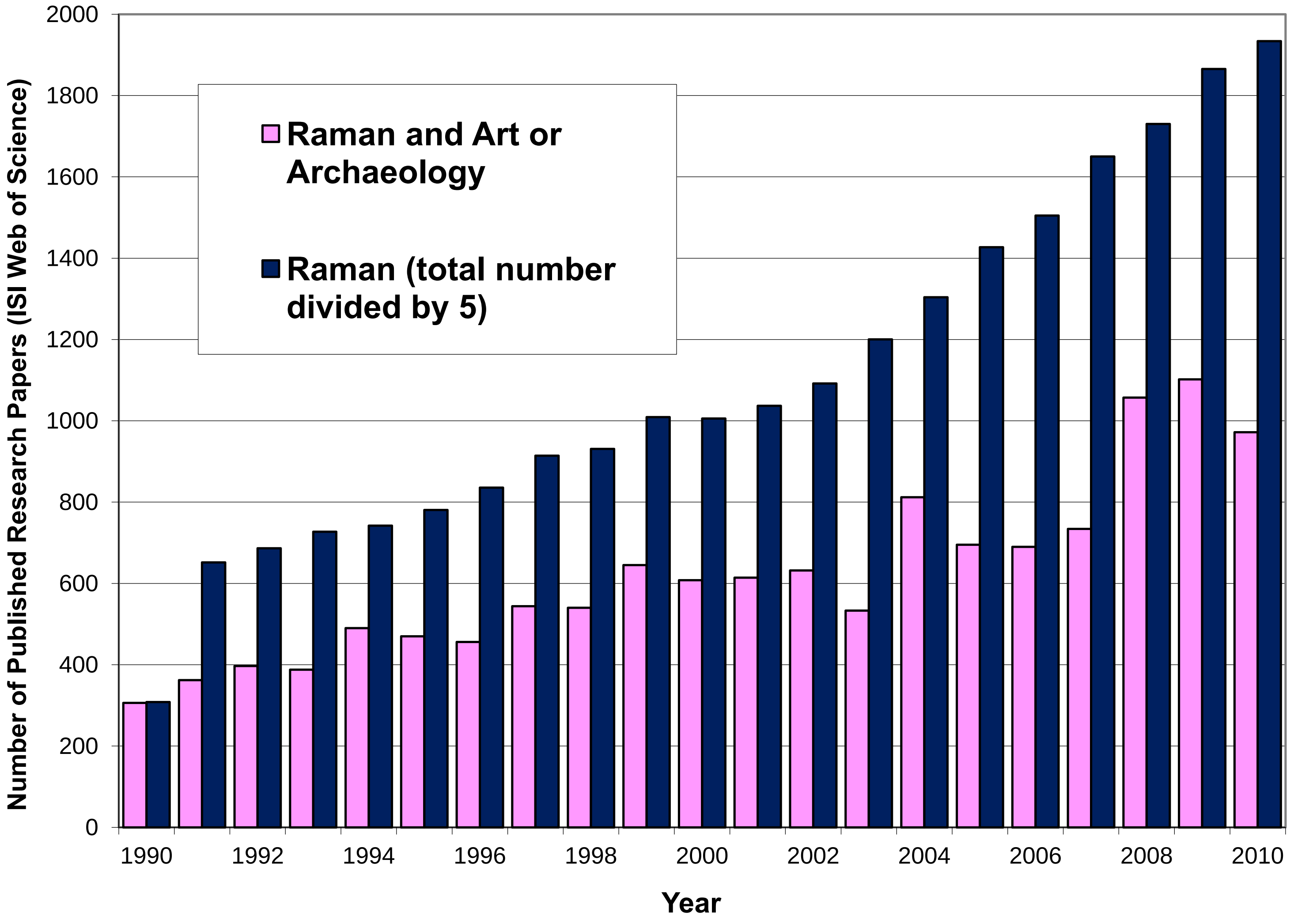
Microsoft Excel

Finished import.

Now please fill in the sample submission information

OK

Increasing use of Raman



Need For a Raman DB

- Complementary to FTIR
- Well suited for many components of cultural heritage
- At IRUG conference (2010):
  - 29% of papers were devoted to Raman
  - 43% to FTIR
  - 28% included both techniques

Raman Review Committee Established

Lucia Burgio	Victoria & Albert Museum
Silvia Centeno	Metropolitan Museum of Art, New York
Suzan de Groot	Netherlands Cultural Heritage Agency
Howell G. Edwards	University of Bradford
Richard Hark	Juniata College
Catherine Higgitt	British Museum
Deborah Lau	CSIRO, Australia
Suzanne Lomax	National Gallery of Art, Washington
Richard Newman	Museum of Fine Arts, Boston
Odile Madden	Smithsonian Insitution
Jennifer Mass	Winterthur Museum
Marcello Picollo	IFAC, Nello Carrara, CNR
Boris Pretzel	Victoria & Albert Museum
Beth Price	Philadelphia Museum of Art
Anna Schőnemann	ABK, Stuttgart
Gregory Smith	Indianapolis Museum of Art
Karen Trentelman	Getty Conservation Institute

2009 IMLS Grant:
IRUG Raman Spectral DB Initiative

- **Awarded by IMLS (Washington DC) to PMA w/ IRUG**
- **Total amount $239,650 with partial match from PMA**
- **Create publicly accessible, Raman DB specific to museum community**
- **Maintain DB on re-tooled IRUG website**
- **Modeled after the IRUG IR DB**
- **Original 2 year grant extended**

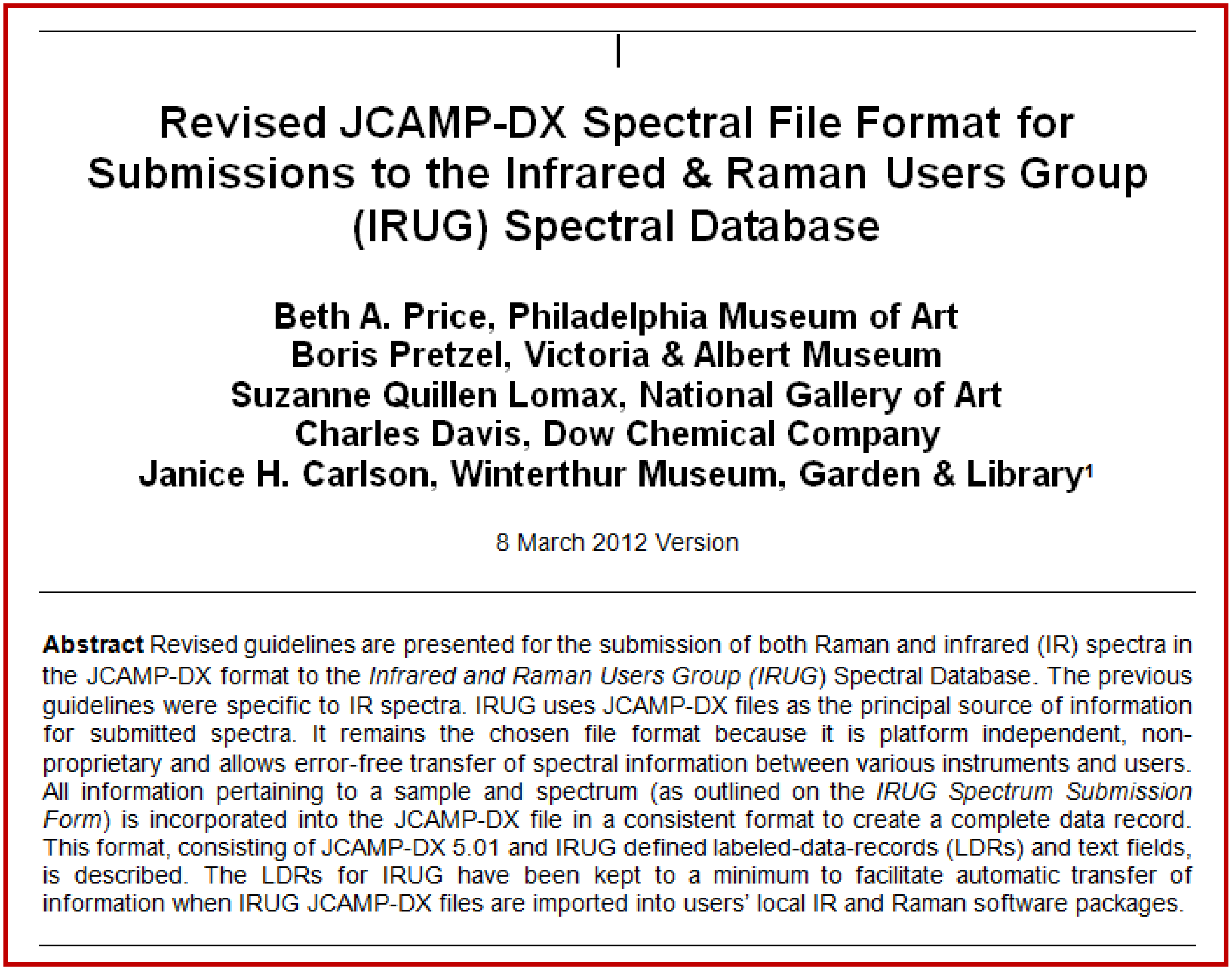
IRUG

INSTITUTE of Museum and Library SERVICES

Project Plans - Key Deliverables

1. DB: archive Raman & IR spectra on www.irug.org
2. Web interface: upload & submit raw JCAMP-DX files, supporting info.
3. Translator: convert raw files to IRUG JCAMP-DX standard files
4. Software: peer-review, transfer approved data to DB
5. DB Interface: online keyword & spectra DB search, data download, printing
6. Bibliography: citations, open source papers, chem. structures
7. Enhancements: updated IR DB, redesigned website, increased security, new features

See: IRUG White Paper for File Format Details



Revised JCAMP-DX Spectral File Format for Submissions to the Infrared & Raman Users Group (IRUG) Spectral Database

Beth A. Price, Philadelphia Museum of Art
Boris Pretzel, Victoria & Albert Museum
Suzanne Quillen Lomax, National Gallery of Art
Charles Davis, Dow Chemical Company
Janice H. Carlson, Winterthur Museum, Garden & Library[1]

8 March 2012 Version

Abstract Revised guidelines are presented for the submission of both Raman and infrared (IR) spectra in the JCAMP-DX format to the *Infrared and Raman Users Group (IRUG)* Spectral Database. The previous guidelines were specific to IR spectra. IRUG uses JCAMP-DX files as the principal source of information for submitted spectra. It remains the chosen file format because it is platform independent, non-proprietary and allows error-free transfer of spectral information between various instruments and users. All information pertaining to a sample and spectrum (as outlined on the *IRUG Spectrum Submission Form*) is incorporated into the JCAMP-DX file in a consistent format to create a complete data record. This format, consisting of JCAMP-DX 5.01 and IRUG defined labeled-data-records (LDRs) and text fields, is described. The LDRs for IRUG have been kept to a minimum to facilitate automatic transfer of information when IRUG JCAMP-DX files are imported into users' local IR and Raman software packages.

IRUG - JCAMP.DX File Format Established

```
##TITLE=RMP00002 Aragonite; Morro Bay, San Luis Obispo; MMHU; 116189; MFAB; scat
##JCAMP-DX=5.01
##DATA TYPE=RAMAN SPECTRUM
##APPLICATION=Raman microspectroscopy
##ORIGIN=institution: Museum of Fine Arts, Boston; address: 465 Huntington
Avenue, Boston, MA, 02115,USA; analyst(s): Michele Derrick, Richard Newman;
tel: +1 617 267 9300; fax: +1 617 369 3182; email: mderrick@mfa.org,
rnewman@mfa.org; submitter: Beth Price, Philadelphia Museum of Art;
tel: +1 215 684 7552; fax: +1 215 684 7540; email:bprice@philamuseum.org
##OWNER=COPYRIGHT © 2008 BY Museum of Fine Arts, Boston
DATABASE COPYRIGHT © 2010 BY Infrared and Raman Users Group (IRUG)
##$LICENSE=By accepting this database user agrees to be bound by the terms of
the IRUG user's license. Any reference written/oral made to this file must
include accreditation to BOTH the originating individual/institution and IRUG.
Contributor agrees to be bound by the terms of the IRUG contributor's license.
##$INSTITUTION FILE NAME=Aragonite (HU Min. Museum 116189), 50X, 785 nm.1.dx
##DATE=08/07/29
##LONGDATE=2008/07/29
##TIME=12:55:37
##SPECTROMETER/DATA SYSTEM=spectrometer: Bruker Optics Senterra RMS;
Spectrometer software: Opus 6.5; detector: CCD; monochromator: dispersive
##INSTRUMENT PARAMETERS=accumulations: 1; purge: N; range: 70-1550 cm-1;
source: 785 nm; power: 9.4 mW; calibration: multiband Neon; data collection:
static; integration time: 30 sec
##RESOLUTION=3-5 cm-1
##DATA PROCESSING=baseline corr.: N; fluorescence corr.: N; cosmic ray removal:
N; detector binning: Y; other data processing: none
```

##DATA PROCESSING=baseline corr.: N; fluorescence corr.: N; cosmic ray removal: N; detector binning: Y; other data processing: none

##SAMPLE DESCRIPTION=mode: scat; accessories: Senterra microscope; support: glass slide; objective magnification: 50x; numerical aperture: 0.75; working distance: 0.38 mm; spot size: 2 microns; confocal: N; angle: 180 degrees backscattered; polarization: N, N; filters: Rayleigh, dielectric; cut-off freq: 89 cm-1; grating type: holographic; grating density: 1200 lines/mm; laser defocus: N

##SAMPLING PROCEDURE=mode: scat; prep: bulk

##PATHLENGTH=

##PRESSURE=

##TEMPERATURE=

##CAS NAME= Aragonite

##NAMES=Aragonite
Calcium carbonate

##MOLFORM=C Ca O3

##$STRUCTFORM=CaCO3

##CAS REGISTRY NUMBER=14791-73-2

##WISWESSER=

##BEILSTEIN LAWSON No=

##MP=Decomposes at 825 degrees C

##BP=

##REFRACTIVE INDEX=1.530, 1.682, 1.686 (literature, cameo.mfa.org)

##DENSITY=2.93-2.95 g/cc (literature, cameo.mfa.org)

##MW=100.09 g/mol (literature, CRC handbook, 59th ed.)

##CONCENTRATIONS=

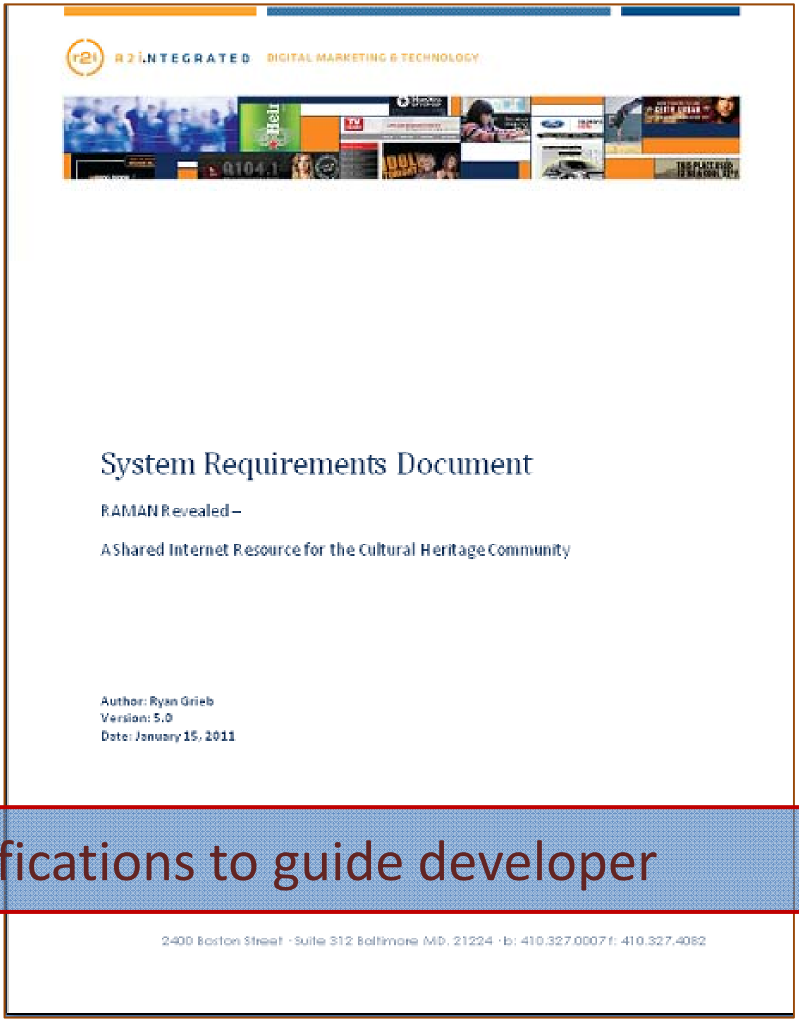
##STATE=state: solid; form: powder

##CROSS REFERENCE=IR spectrum: Aragonite, Ref 116189, Morrow Bay, San Luis Obispo

##$LITERATURE REFERENCE=Howell G. M. Edwards, et al., FT-Raman spectroscopic study of calcium-rich and magnesium-rich carbonate minerals, Spectrochimica Acta Part A 61 (2005) 2273-2280.

##$LITERATURE REFERENCE=Howell G. M. Edwards, et al., FT-Raman spectroscopic study of calcium-rich and magnesium-rich carbonate minerals, Spectrochimica Acta Part A 61 (2005) 2273-2280.
##$OTHER ANALYTICAL METHODS=FTIR, EDS
##$SAMPLE SOURCE 1=Morro Bay
##$SOURCE LOCATION 1=San Luis Obispo, CA, USA
##$SAMPLE IDENTIFIER 1=
##$SAMPLE SOURCE 2=Mineralogical Museum Harvard University (MMHU)
##$SOURCE LOCATION 2=24 Oxford Street, Cambridge, MA, USA
##$SAMPLE IDENTIFIER 2=MMHU# 116189
##$SAMPLE SOURCE 3=Museum of Fine Arts, Boston
##$SOURCE LOCATION 3=465 Huntington Avenue, Boston, MA, 02115
##$SAMPLE IDENTIFIER 3=MFA Ref# 116189
##$COLOR=White
##$AGE=
##$IRUG MATERIALS CLASS=MP
##$OTHER=sample type: reference material
##DELTAX=0.5
##XUNITS=1/CM
##YUNITS=RELATIVE INTENSITY
##FIRSTX=70
##LASTX=1550
##FIRSTY=8123.4546
##MAXY=29326.285
##MINY=689.02875
##XFACTOR=1
##YFACTOR=2.7312231e-005
##NPOINTS=2961
##XYDATA=(X++(Y..Y))
70.00...
##END=

Detailed Systems Requirements Document Completed



R 2 i.NTEGRATED DIGITAL MARKETING & TECHNOLOGY

System Requirements Document

RAMAN Revealed –

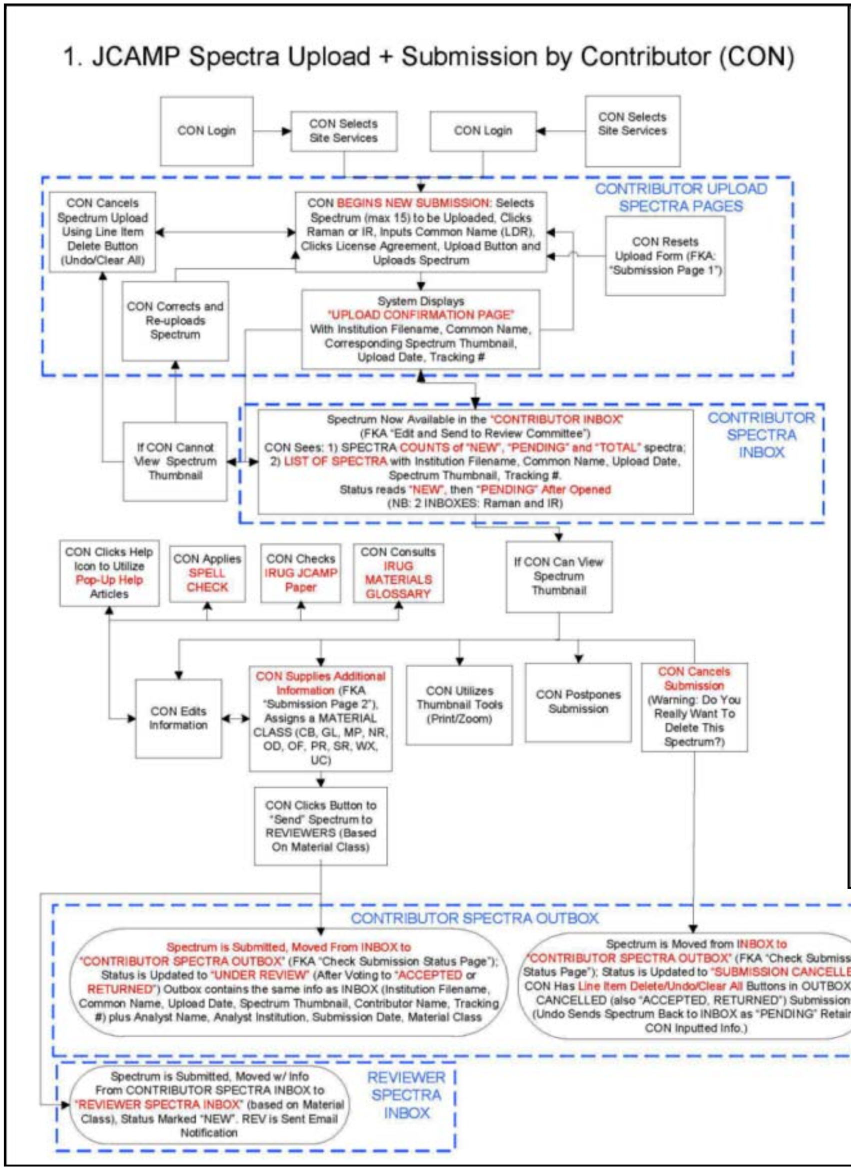
A Shared Internet Resource for the Cultural Heritage Community

Author: Ryan Grieb
Version: 5.0
Date: January 15, 2011

2400 Boston Street · Suite 312 Baltimore MD. 21224 · b: 410.327.0007 f: 410.327.4082

46 pages of specifications to guide developer

Detailed Work Flows Established



1. JCAMP Spectra Upload + Submission by Contributor (CON)

CON Login

CON Selects Site Services

CON Login

CON Selects Site Services

CONTRIBUTOR UPLOAD SPECTRA PAGES

CON Cancels Spectrum Upload Using Line Item Delete Button (Undo/Clear All)

CON BEGINS NEW SUBMISSION: Selects Spectrum (max 15) to be Uploaded, Clicks Raman or IR, Inputs Common Name (LDR), Clicks License Agreement, Upload Button and Uploads Spectrum

CON Resets Upload Form (FKA: "Submission Page 1")

CON Corrects and Re-uploads Spectrum

System Displays "UPLOAD CONFIRMATION PAGE" With Institution Filename, Common Name, Corresponding Spectrum Thumbnail, Upload Date, Tracking #

CONTRIBUTOR SPECTRA INBOX

If CON Cannot View Spectrum Thumbnail

Spectrum Now Available in the "CONTRIBUTOR INBOX" (FKA "Edit and Send to Review Committee")
CON Sees: 1) SPECTRA COUNTS of "NEW", "PENDING" and "TOTAL" spectra; 2) LIST OF SPECTRA with Institution Filename, Common Name, Upload Date, Spectrum Thumbnail, Tracking #.
Status reads "NEW", then "PENDING" After Opened
(NB: 2 INBOXES: Raman and IR)

CON Clicks Help Icon to Utilize Pop-Up Help Articles

CON Applies SPELL CHECK

CON Checks IRUG JCAMP Paper

CON Consults IRUG MATERIALS GLOSSARY

If CON Can View Spectrum Thumbnail

CON Edits Information

CON Supplies Additional Information (FKA "Submission Page 2"), Assigns a MATERIAL CLASS (CB, GL, MP, NR, OD, OF, PR, SR, WX, UC)

CON Utilizes Thumbnail Tools (Print/Zoom)

CON Postpones Submission

CON Cancels Submission (Warning: Do You Really Want To Delete This Spectrum?)

CON Clicks Button to "Send" Spectrum to REVIEWERS (Based On Material Class)

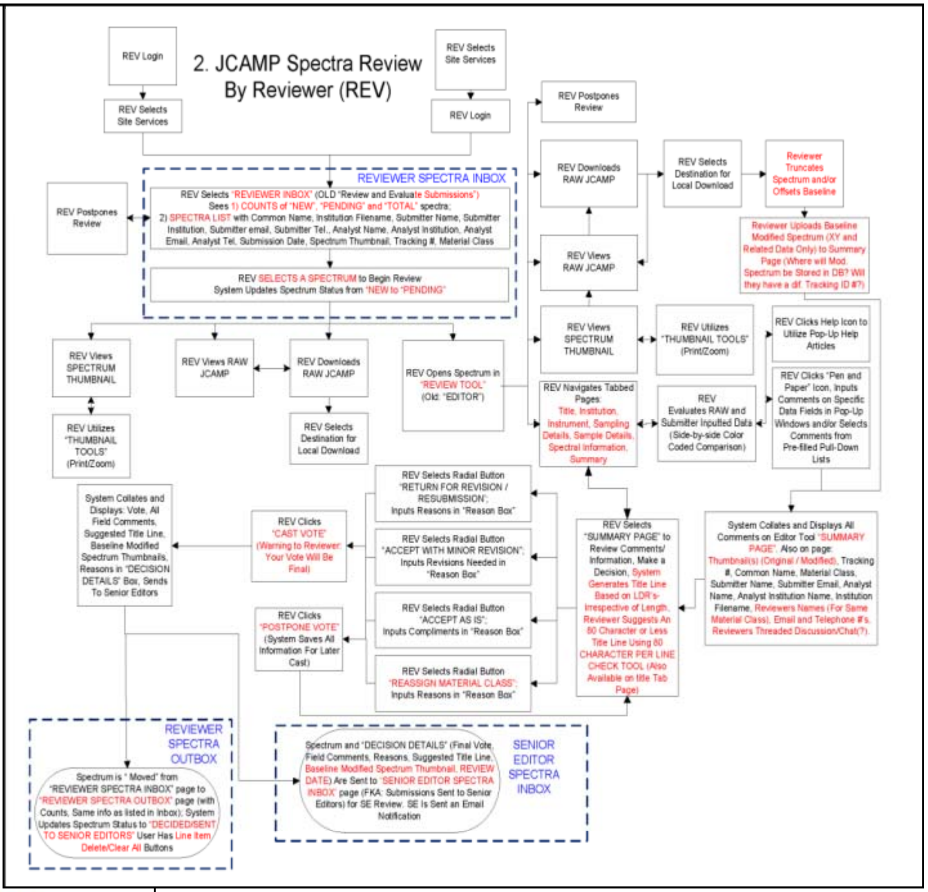
CONTRIBUTOR SPECTRA OUTBOX

Spectrum is Submitted, Moved From INBOX to "CONTRIBUTOR SPECTRA OUTBOX" (FKA "Check Submission Status Page"); Status is Updated to "UNDER REVIEW" (After Voting to "ACCEPTED or RETURNED") Outbox contains the same info as INBOX (Institution Filename, Common Name, Upload Date, Spectrum Thumbnail, Contributor Name, Tracking #) plus Analyst Name, Analyst Institution, Submission Date, Material Class

Spectrum is Moved from INBOX to "CONTRIBUTOR SPECTRA OUTBOX" (FKA "Check Submission Status Page"); Status is Updated to "SUBMISSION CANCELLED". CON Has Line Item Delete/Undo/Clear All Buttons in OUTBOX for CANCELLED (also "ACCEPTED, RETURNED") Submissions (Undo Sends Spectrum Back to INBOX as "PENDING" Retains CON Inputted Info.)

REVIEWER SPECTRA INBOX

Spectrum is Submitted, Moved w/ Info From CONTRIBUTOR SPECTRA INBOX to "REVIEWER SPECTRA INBOX" (based on Material Class), Status Marked "NEW". REV is Sent Email Notification



2. JCAMP Spectra Review By Reviewer (REV)

REV Login

REV Selects Site Services

REV Selects Site Services

REV Login

REVIEWER SPECTRA INBOX

REV Postpones Review

REV Selects "REVIEWER INBOX" (OLD "Review and Evaluate Submissions")
Sees 1) COUNTS of "NEW", "PENDING" and "TOTAL" spectra;
2) SPECTRA LIST with Common Name, Institution Filename, Submitter Name, Submitter Institution, Submitter email, Submitter Tel., Analyst Name, Analyst Institution, Analyst Email, Analyst Tel, Submission Date, Spectrum Thumbnail, Tracking #, Material Class

REV SELECTS A SPECTRUM to Begin Review
System Updates Spectrum Status from "NEW to "PENDING"

REV Views SPECTRUM THUMBNAIL

REV Utilizes "THUMBNAIL TOOLS" (Print/Zoom)

REV Views RAW JCAMP

REV Downloads RAW JCAMP

REV Selects Destination for Local Download

REV Opens Spectrum in "REVIEW TOOL" (Old: "EDITOR")

REV Postpones Review

REV Downloads RAW JCAMP

REV Selects Destination for Local Download

Reviewer Truncates Spectrum and/or Offsets Baseline

Reviewer Uploads Baseline Modified Spectrum (XY and Related Data Only) to Summary Page (Where will Mod. Spectrum be Stored in DB? Will they have a dif. Tracking ID #?)

REV Views RAW JCAMP

REV Views SPECTRUM THUMBNAIL

REV Utilizes "THUMBNAIL TOOLS" (Print/Zoom)

REV Clicks Help Icon to Utilize Pop-Up Help Articles

REV Navigates Tabbed Pages: Title, Institution, Instrument, Sampling Details, Sample Details, Spectral Information, Summary

REV Evaluates RAW and Submitter Inputted Data (Side-by-side Color Coded Comparison)

REV Clicks "Pen and Paper" Icon, Inputs Comments on Specific Data Fields in Pop-Up Windows and/or Selects Comments from Pre-filled Pull-Down Lists

System Collates and Displays: Vote, All Field Comments, Suggested Title Line, Baseline Modified Spectrum Thumbnails, Reasons in "DECISION DETAILS" Box, Sends To Senior Editors

REV Clicks "CAST VOTE" (Warning to Reviewer: Your Vote Will Be Final)

REV Clicks "POSTPONE VOTE" (System Saves All Information For Later Cast)

REV Selects Radial Button "RETURN FOR REVISION / RESUBMISSION"; Inputs Reasons in "Reason Box"

REV Selects Radial Button "ACCEPT WITH MINOR REVISION"; Inputs Revisions Needed in "Reason Box"

REV Selects Radial Button "ACCEPT AS IS"; Inputs Compliments in "Reason Box"

REV Selects Radial Button "REASSIGN MATERIAL CLASS"; Inputs Reasons in "Reason Box"

REV Selects "SUMMARY PAGE" to Review Comments/ Information, Make a Decision, System Generates Title Line Based on LDR's-Irrespective of Length, Reviewer Suggests An 80 Character or Less Title Line Using 80 CHARACTER PER LINE CHECK TOOL (Also Available on title Tab Page)

System Collates and Displays All Comments on Editor Tool "SUMMARY PAGE". Also on page: Thumbnail(s) (Original / Modified), Tracking #, Common Name, Material Class, Submitter Name, Submitter Email, Analyst Name, Analyst Institution Name, Institution Filename, Reviewers Names (For Same Material Class), Email and Telephone #'s, Reviewers Threaded Discussion/Chat(?).

REVIEWER SPECTRA OUTBOX

Spectrum is " Moved" from "REVIEWER SPECTRA INBOX" page to "REVIEWER SPECTRA OUTBOX" page (with Counts, Same info as listed in Inbox); System Updates Spectrum Status to "DECIDED/SENT TO SENIOR EDITORS" User Has Line Item Delete/Clear All Buttons

SENIOR EDITOR SPECTRA INBOX

Spectrum and "DECISION DETAILS" (Final Vote, Field Comments, Reasons, Suggested Title Line, Baseline Modified Spectrum Thumbnail, REVIEW DATE) Are Sent to "SENIOR EDITOR SPECTRA INBOX" page (FKA: Submissions Sent to Senior Editors) for SE Review. SE Is Sent an Email Notification

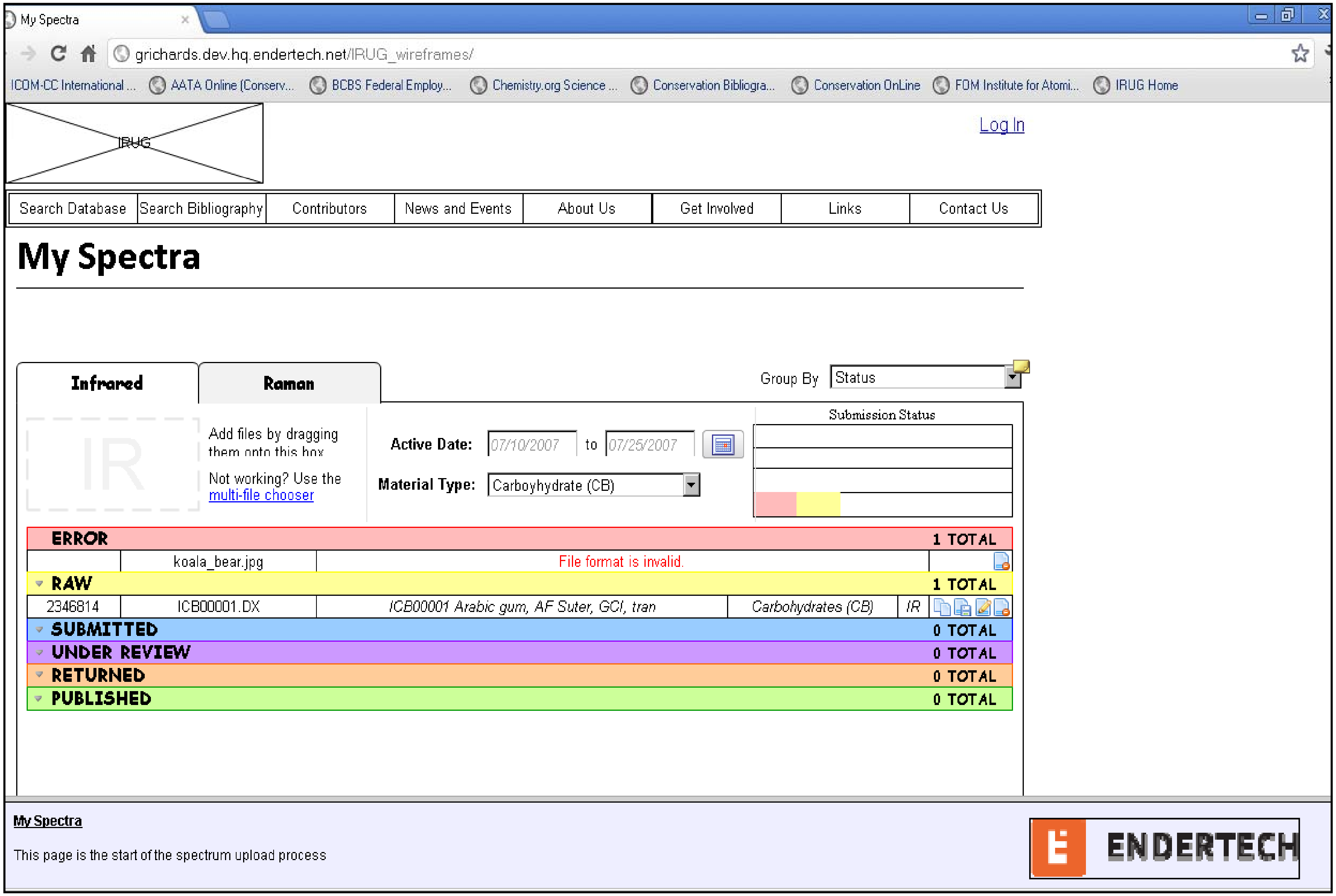
Shown are 2 of 14 blueprints for the developer

Pre-Build Spectra Pledged

Org pigments, 20th-21st C.	N. Scherrer	Bern University of the Arts
Early synthetic dyes	S. de Groot	RCE (formerly ICN)
Gems	D. Bersani	University of Parma
Pigments	F. Casadio	Art Institute of Chicago
Lapis lazuli	R. Hark	Juniata College
The Resin Kit	G. Smith	Indianapolis Museum of Art
Plastics, bone, teeth, tortoiseshell, aged conservation materials	O. Madden	Smithsonian Institute
Logwood inks, syn. organic pigments	S. Centeno	Metropolitan Museum of Art
Syn. org. Tate & Forbes pigments	J. Mass, C. Matsen	Winterthur Museum
Winsor & Newton watercolors,19th C.	L. Burgio	Victoria and Albert Museum
Dry pigments	D. Lau	CSIRO, Australia
Tate Collection pigments. others	R. Newman	Museum of Fine Arts, Boston
Synthetic organic pigments	S. Lomax	National Gallery of Art
Forbes Pigments	B. Price	Phildelphia Museum of Art

Over 1000 spectra have been collected

Wireframes Developed - Dashboard



My Spectra

Add files by dragging them onto this box

Not working? Use the multi-file chooser

Active Date: 07/10/2007 to 07/25/2007

Material Type: Carboyhydrate (CB)

Group By: Status

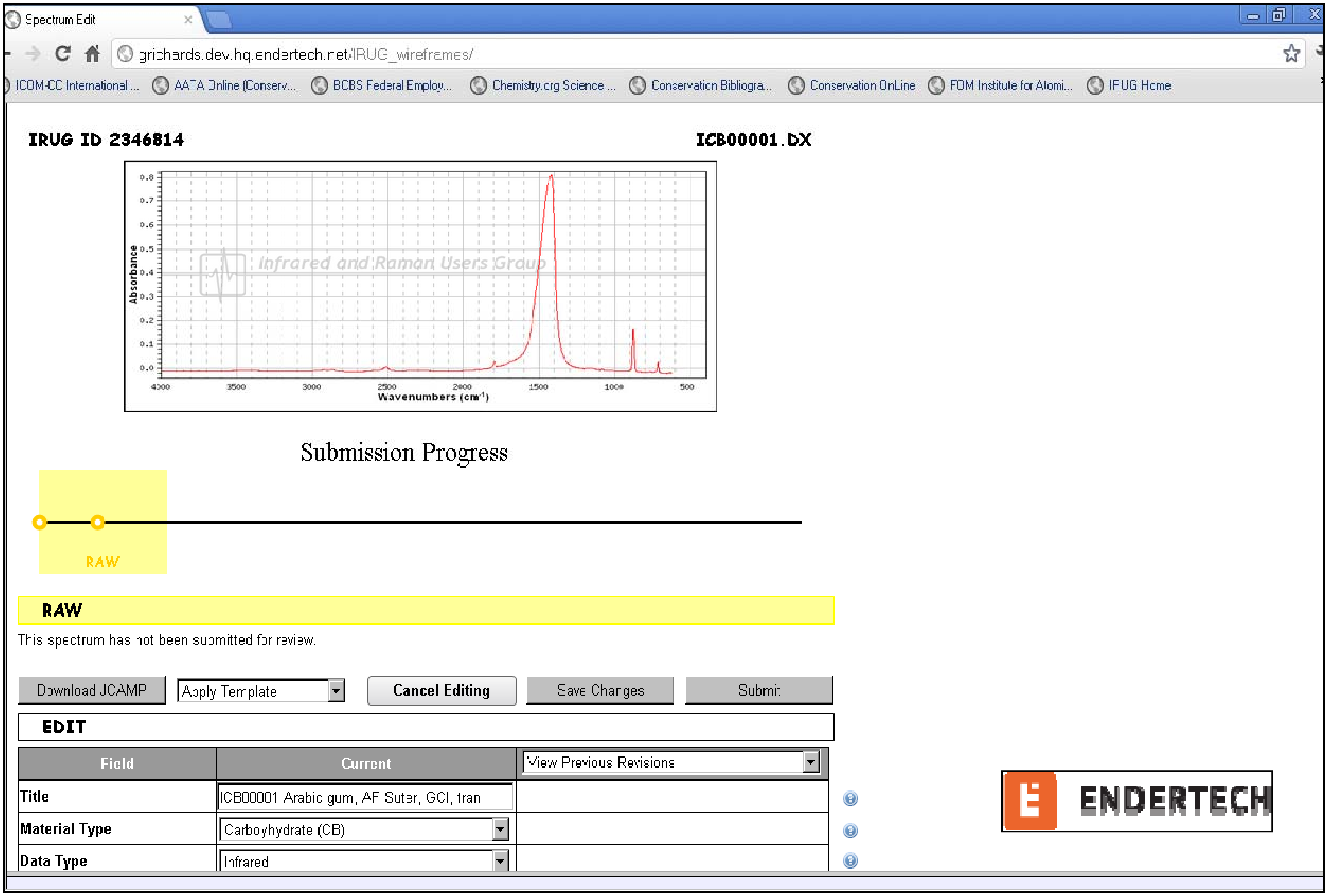
ERROR					**1 TOTAL**
	koala_bear.jpg	File format is invalid.			
RAW					**1 TOTAL**
2346814	ICB00001.DX	*ICB00001 Arabic gum, AF Suter, GCI, tran*	*Carbohydrates (CB)*	*IR*	
SUBMITTED					**0 TOTAL**
UNDER REVIEW					**0 TOTAL**
RETURNED					**0 TOTAL**
PUBLISHED					**0 TOTAL**

My Spectra

This page is the start of the spectrum upload process

ENDERTECH

Wireframes - Spectral Submission



IRUG ID 2346814

ICB00001.DX

Submission Progress

RAW

RAW

This spectrum has not been submitted for review.

EDIT

Field	Current	View Previous Revisions
Title	ICB00001 Arabic gum, AF Suter, GCI, tran	
Material Type	Carboyhydrate (CB)	
Data Type	Infrared	

IRUG spectral search

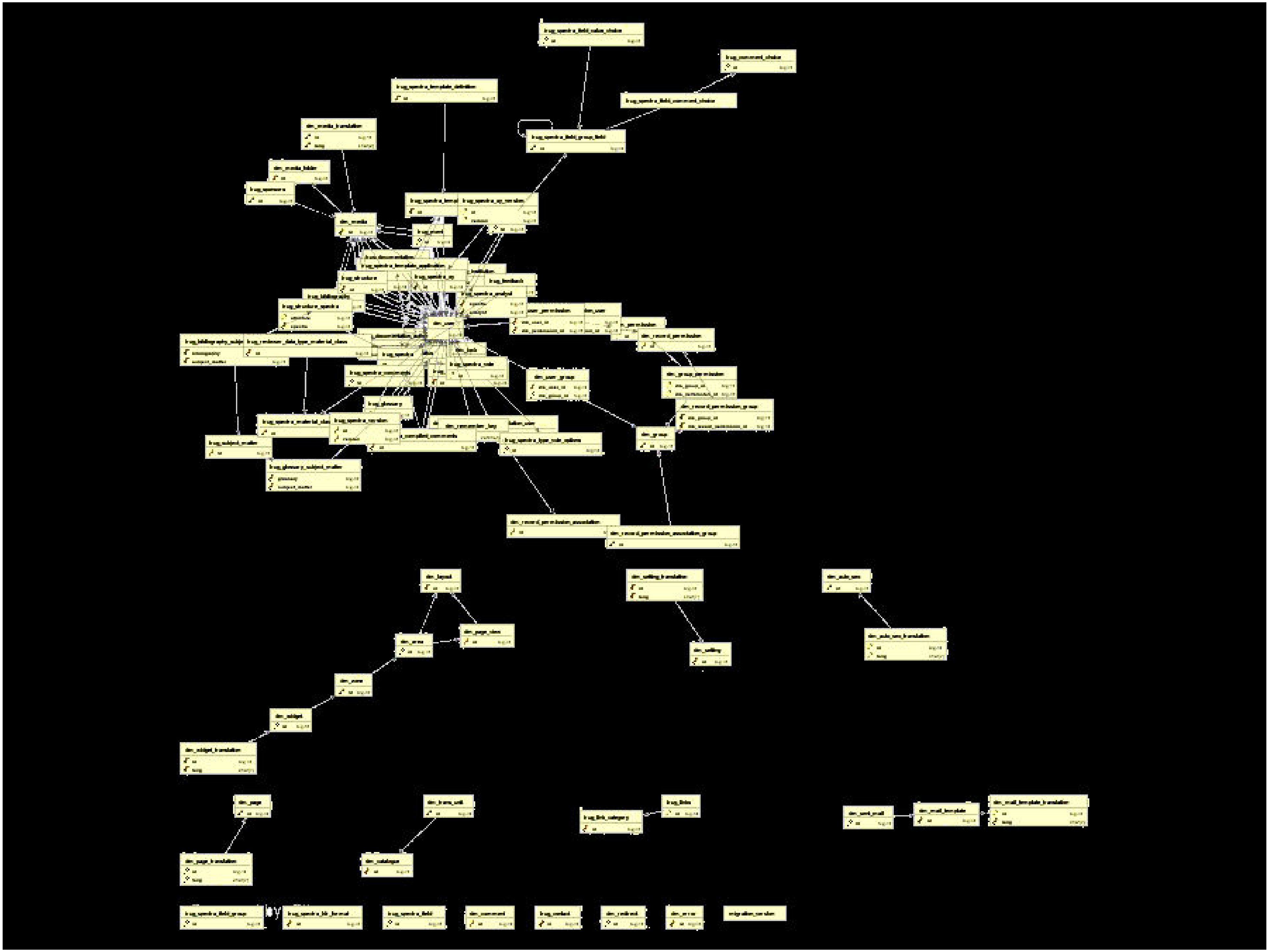
Welcome admin_editor (admin_editor)

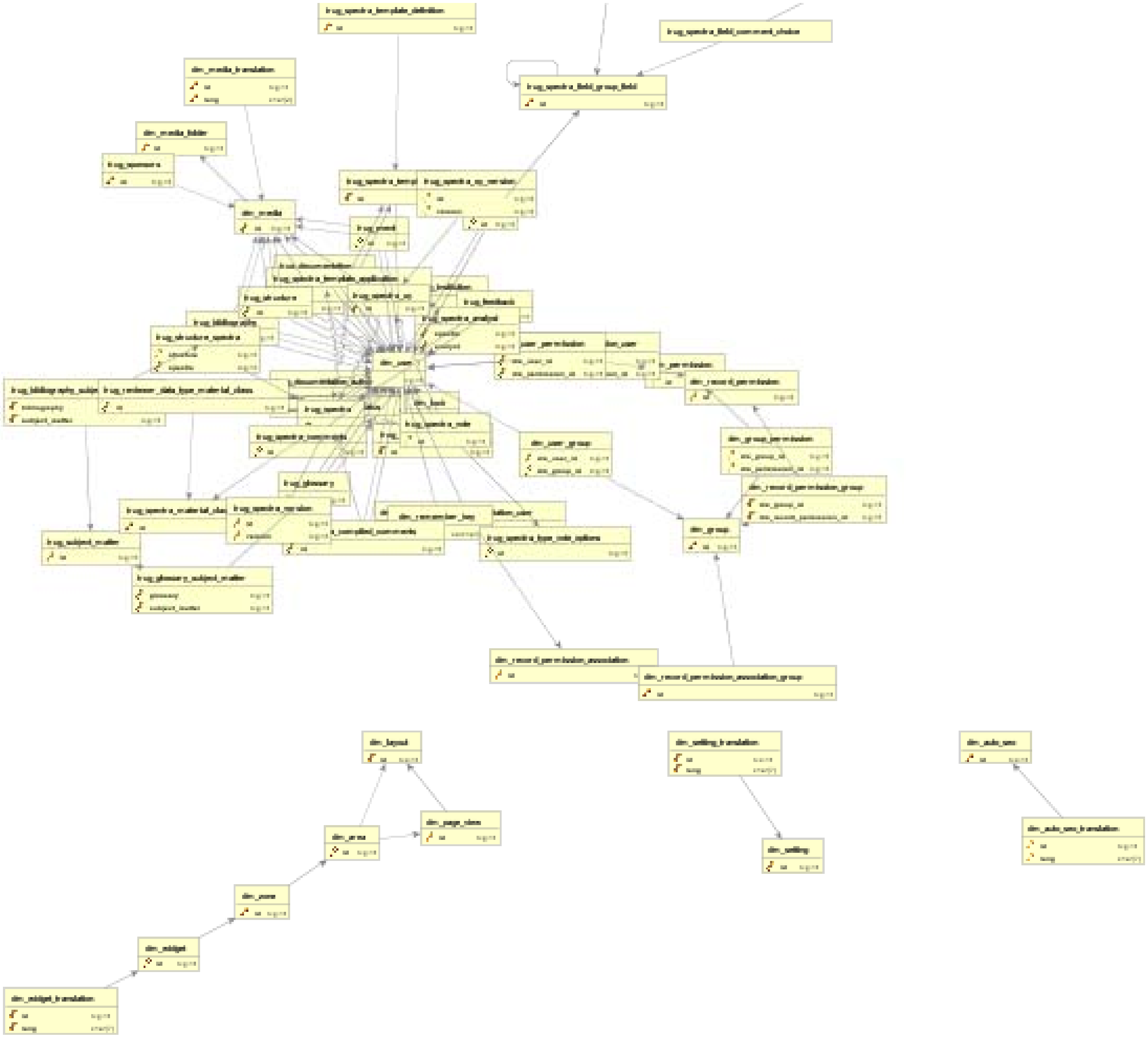
Spectral

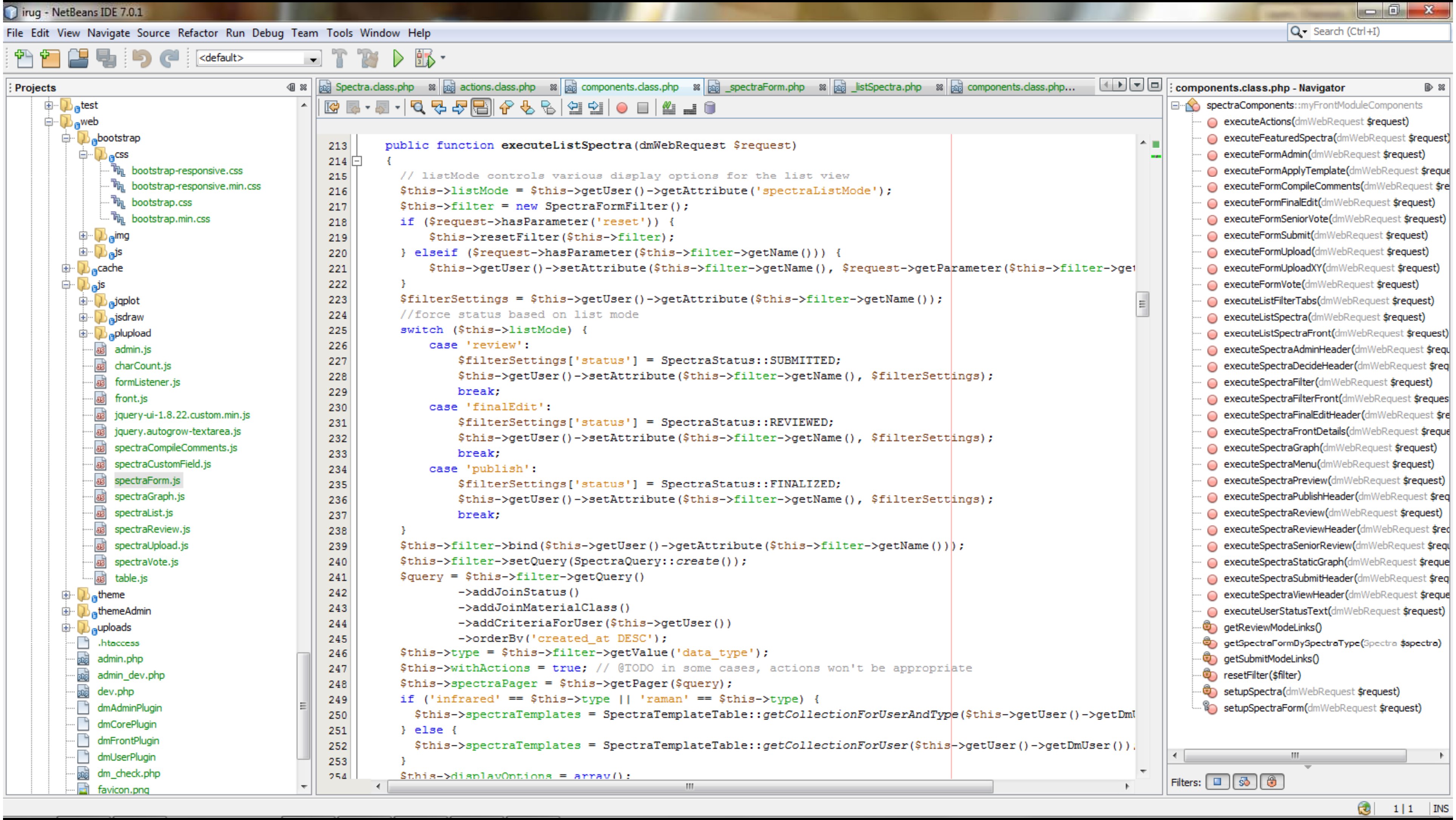
☑ I have read the terms of use…

ID: 2289 - IMP00330 whewellite, Aldrich, #289841, PMA, tran

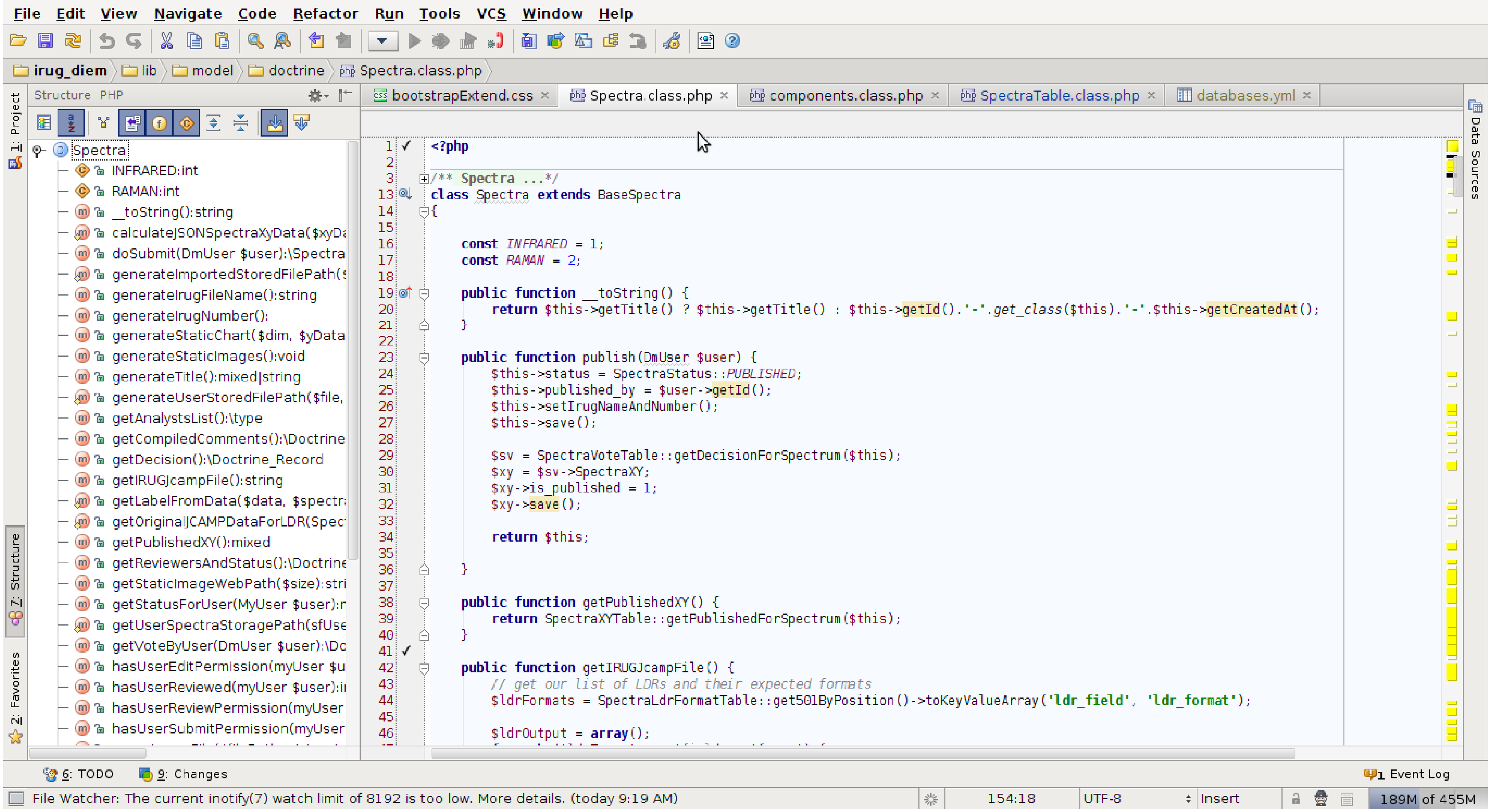
Spectra XY Upload Form ID: 2289




dm_media_translation
dm_media_folder
dm_media
dm_user
dm_user_permission
dm_record_permission
dm_group_permission
dm_record_permission_group
dm_user_group
dm_group
dm_record_permission_association
dm_record_permission_association_group
dm_layout
dm_area
dm_page_view
dm_zone
dm_widget
dm_widget_translation
dm_setting_translation
dm_setting
dm_auto_seo
dm_auto_seo_translation
dm_remember_key
id
lang
bigint
varchar



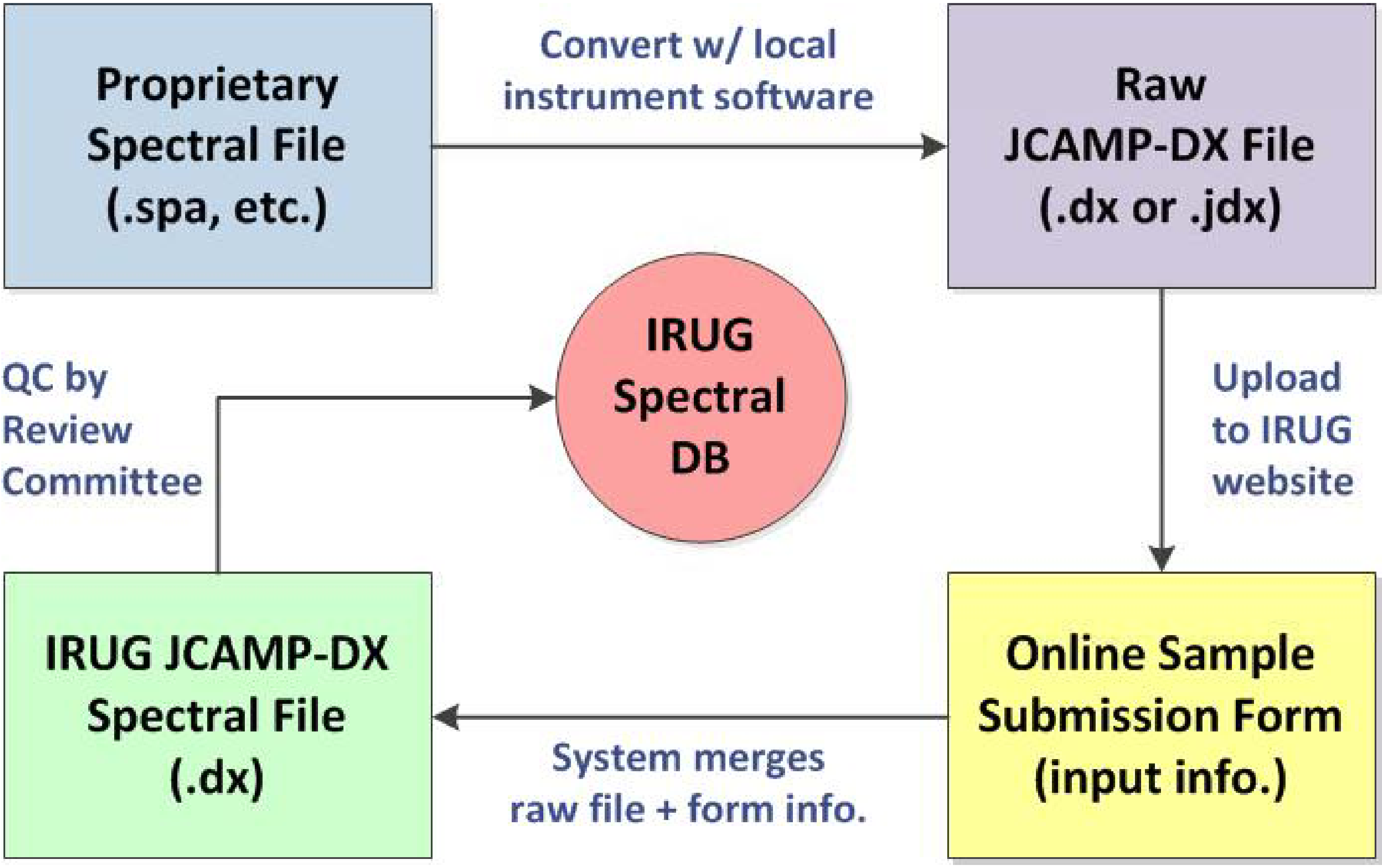
```php
    public function executeListSpectra(dmWebRequest $request)
    {
      // listMode controls various display options for the list view
      $this->listMode = $this->getUser()->getAttribute('spectraListMode');
      $this->filter = new SpectraFormFilter();
      if ($request->hasParameter('reset')) {
          $this->resetFilter($this->filter);
      } elseif ($request->hasParameter($this->filter->getName())) {
          $this->getUser()->setAttribute($this->filter->getName(), $request->getParameter($this->filter->get
      }
      $filterSettings = $this->getUser()->getAttribute($this->filter->getName());
      //force status based on list mode
      switch ($this->listMode) {
          case 'review':
              $filterSettings['status'] = SpectraStatus::SUBMITTED;
              $this->getUser()->setAttribute($this->filter->getName(), $filterSettings);
              break;
          case 'finalEdit':
              $filterSettings['status'] = SpectraStatus::REVIEWED;
              $this->getUser()->setAttribute($this->filter->getName(), $filterSettings);
              break;
          case 'publish':
              $filterSettings['status'] = SpectraStatus::FINALIZED;
              $this->getUser()->setAttribute($this->filter->getName(), $filterSettings);
              break;
      }
      $this->filter->bind($this->getUser()->getAttribute($this->filter->getName()));
      $this->filter->setQuery(SpectraQuery::create());
      $query = $this->filter->getQuery()
              ->addJoinStatus()
              ->addJoinMaterialClass()
              ->addCriteriaForUser($this->getUser())
              ->orderBy('created_at DESC');
      $this->type = $this->filter->getValue('data_type');
      $this->withActions = true; // @TODO in some cases, actions won't be appropriate
      $this->spectraPager = $this->getPager($query);
      if ('infrared' == $this->type || 'raman' == $this->type) {
        $this->spectraTemplates = SpectraTemplateTable::getCollectionForUserAndType($this->getUser()->getDm
      } else {
        $this->spectraTemplates = SpectraTemplateTable::getCollectionForUser($this->getUser()->getDmUser())
      }
      $this->displayOptions = array();
```



```php
<?php

/** Spectra ...*/
class Spectra extends BaseSpectra
{

    const INFRARED = 1;
    const RAMAN = 2;

    public function __toString() {
        return $this->getTitle() ? $this->getTitle() : $this->getId().'-'.get_class($this).'-'.$this->getCreatedAt();
    }

    public function publish(DmUser $user) {
        $this->status = SpectraStatus::PUBLISHED;
        $this->published_by = $user->getId();
        $this->setIrugNameAndNumber();
        $this->save();

        $sv = SpectraVoteTable::getDecisionForSpectrum($this);
        $xy = $sv->SpectraXY;
        $xy->is_published = 1;
        $xy->save();

        return $this;

    }

    public function getPublishedXY() {
        return SpectraXYTable::getPublishedForSpectrum($this);
    }

    public function getIRUGJcampFile() {
        // get our list of LDRs and their expected formats
        $ldrFormats = SpectraLdrFormatTable::get501ByPosition()->toKeyValueArray('ldr_field', 'ldr_format');

        $ldrOutput = array();
```

File Watcher: The current inotify(7) watch limit of 8192 is too low. More details. (today 9:19 AM)

Overview of File Submission Sequence



Proprietary Spectral File (.spa, etc.)

Convert w/ local instrument software

Raw JCAMP-DX File (.dx or .jdx)

Upload to IRUG website

Online Sample Submission Form (input info.)

System merges raw file + form info.

IRUG JCAMP-DX Spectral File (.dx)

QC by Review Committee

IRUG Spectral DB

Acknowledgements

Institute of Museum and Library Services

National Center for Preservation Training & Technology

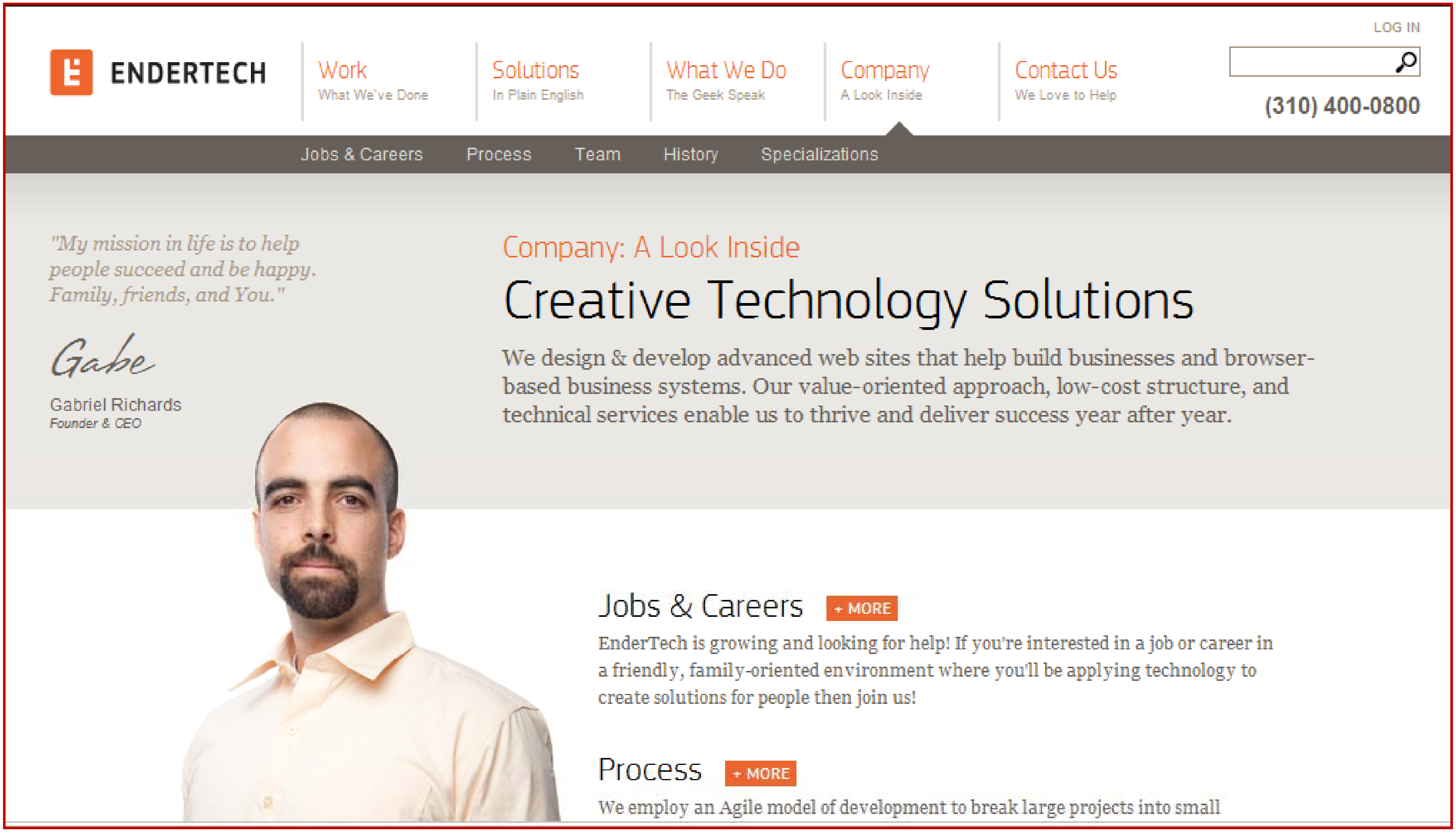
The Dow Chemical Company

Saint Gobain Corporation Foundation

Samuel H. Kress Foundation

PMA, NGA (DC), V&A, IFAC-CNR

All IRUG Contributors and Reviewers



"My mission in life is to help people succeed and be happy. Family, friends, and You."

Gabe

Gabriel Richards
Founder & CEO

Company: A Look Inside

Creative Technology Solutions

We design & develop advanced web sites that help build businesses and browser-based business systems. Our value-oriented approach, low-cost structure, and technical services enable us to thrive and deliver success year after year.

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EnderTech is growing and looking for help! If you're interested in a job or career in a friendly, family-oriented environment where you'll be applying technology to create solutions for people then join us!

Process

We employ an Agile model of development to break large projects into small

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Discussion & Questions

Marcello Picollo

Institute of Applied Physics “Nello Carrara”, National Research Council,

Florence, IT

THURSDAY, SEPTEMBER 29: DISCUSSION & QUESTIONS

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Synthetic organic pigments: structures & properties

Suzanne Lomax

National Gallery of Art, Washington, D.C., US

FRIDAY, SEPTEMBER 28: LECTURE 1

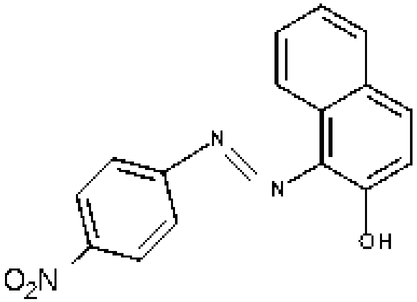
Synthetic Organic Pigments: Structures and Properties

Suzanne Quillen Lomax
National Gallery of Art
Washington DC

Colour Index system of nomenclature

- Web publication of the Society of Dyers and Colourists
- Applies to both organic and inorganic pigments
- Each pigment is assigned a Colour Index name and number
- Example of name is PR1 (for Pigment Red 1)
- Example of number is 12070 for PR1
- Number is usually five digits, but can be six

PR1, 12070
Para Red



Dye vs Pigment

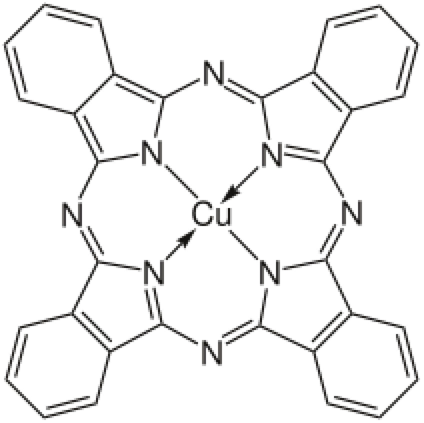
- Pigments are colored, black, white or fluorescent particulate organic and inorganic solids which usually are insoluble in the vehicle or substrate in which they are incorporated.* Pigments retain a crystal or particulate structure.
- Dyes penetrate the substrate in a soluble form and then may become insoluble.
- A Lake is an organic colorant that has been combined with an inorganic substrate or extender.

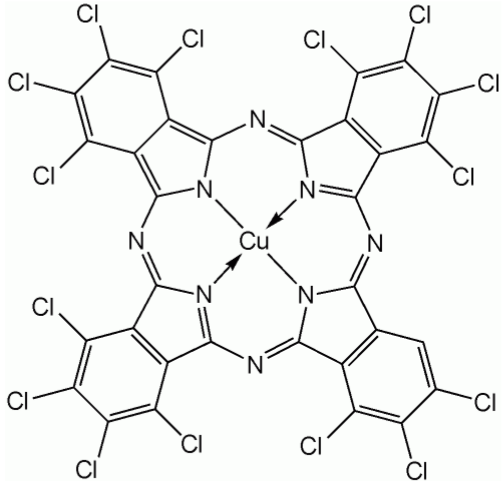
*Dry Color Manufacturers' Association definition

Chromophore and Auxochromes

- Chromophore—a characteristic grouping or arrangement of atoms that imparts color to the molecule
- Auxochrome—(auxiliary chromophore), modifying groups which alter the appearance of the primary hue of the pigment

PB15





PG7

Color, continued.

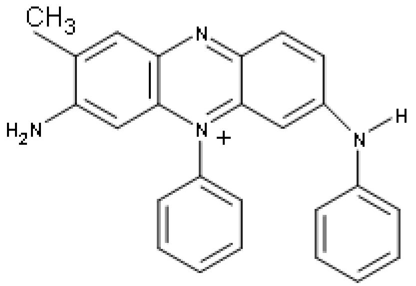
- Color is also affected by:
    - Particle size distribution
    - Polymorphic crystal modification

Different polymorphs of **PV19**

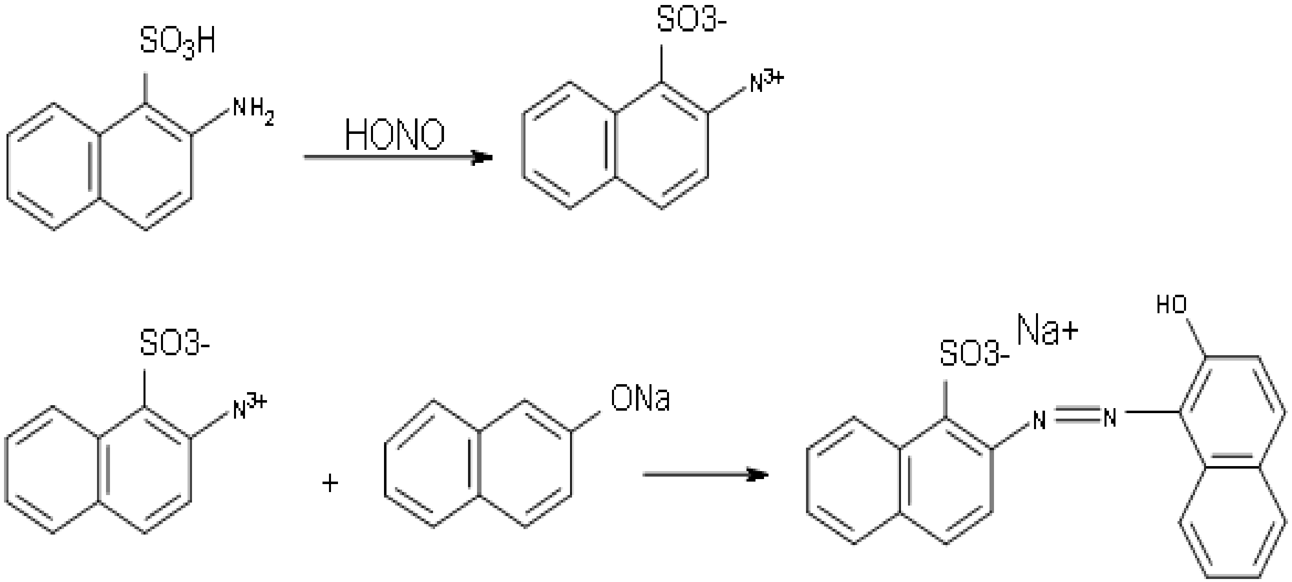
Early Synthetic Organic Pigment History

- 1856 Perkin discovers synthetic mauve

Mauveine A



- Diazotization reaction discovered 1858 by Peter Griess



Sodium Lithol Red
PR49

Early Synthetic Organic Dyes and Pigments

From ***Bright Earth: Art and the Invention of Color by Philip Ball, 2001***

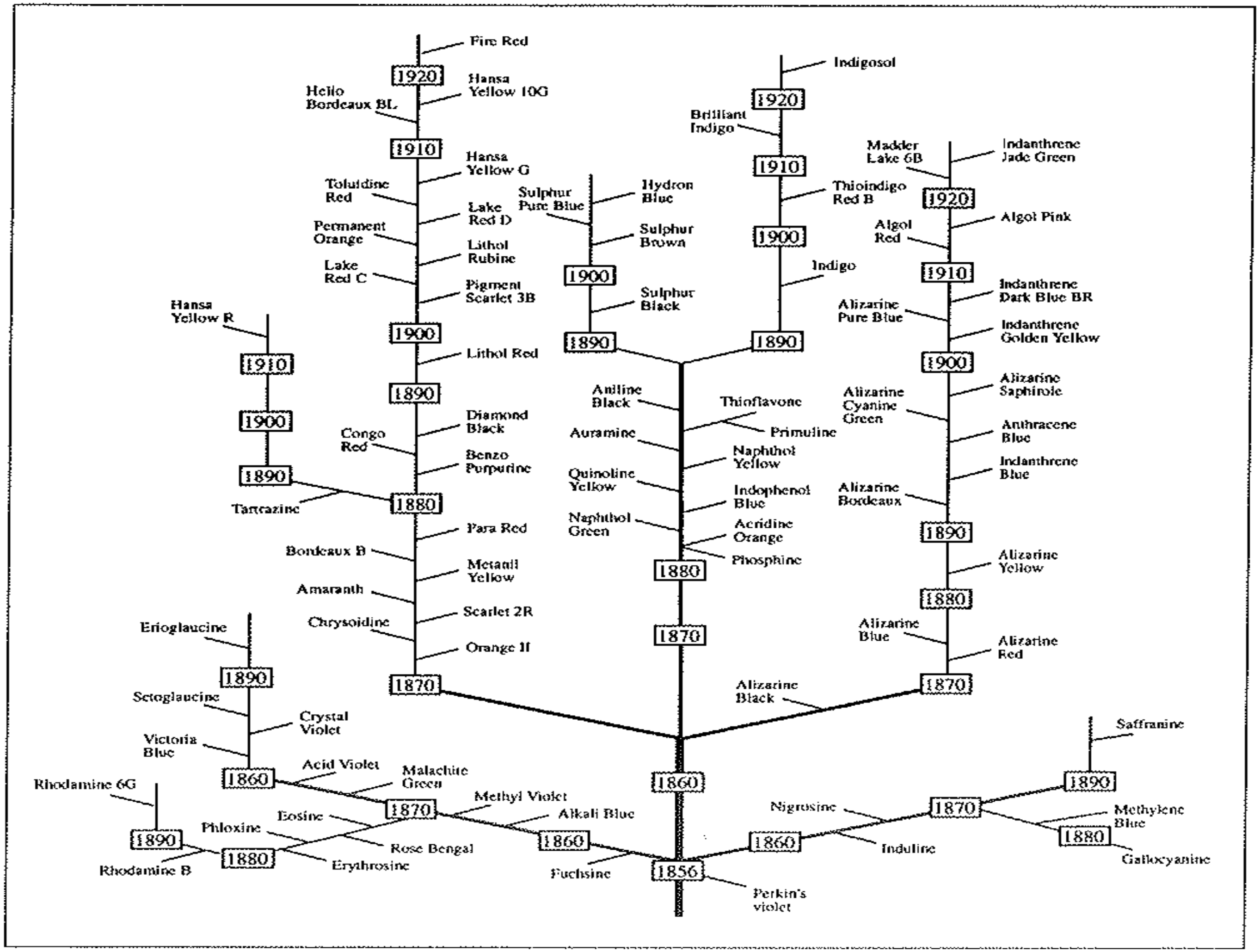
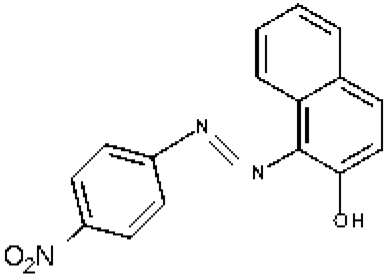


Figure 9.1: Coal-tar and related organic colors proliferated with dizzying variety by the early twentieth century.

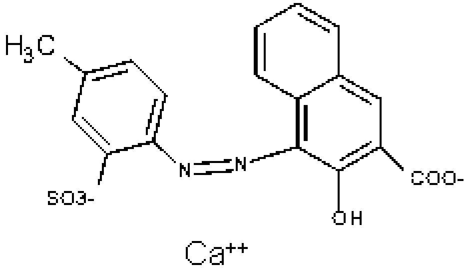
Early Synthetic Organic Pigments

EARLY AZO BASED YELLOWS AND REDS

- 1884 Tartrazine yellow (PY100, pyrazolone)
- 1885 Para Red (PR1, β–naphthol)
- 1899 Lithol Red (PR49, β-naphthol)
- 1903 Lithol Rubine (PR57, BONA)
- 1905 Toluidine Red (PR3, β–naphthol)
- 1907 BON Maroon (PR63, BONA)
- 1909 Dinitroaniline orange (PO5, β–naphthol)



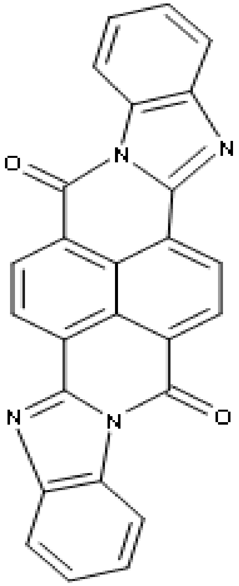
PR1



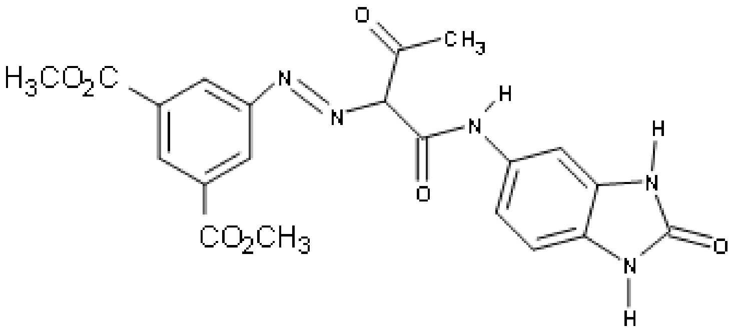
PR57:1

More Recent Synthetic Organic Pigments

- 1909 Hansa (Arylide) yellows
- 1911 Diarylide yellows & oranges
- 1935 Phthalocyanine blue
- 1938 Phthalocyanine green
- 1950 Perylenes and perinones
- 1955 Quinacridones
- 1957 Disazo condensation
- 1960 Benzimidazolones
- 1980s DPP pigments



PO43
perinone

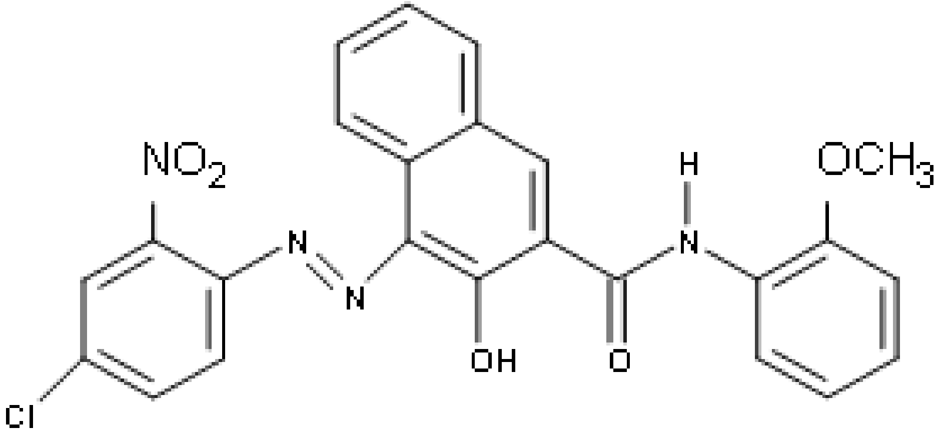


PY120
benzimidazolone

Fastness Properties

- In azo pigments, light and weather fastness is improved by electron accepting groups (halogens, nitro, CO_2R) on the diazo component and electron donating groups (methyl or methoxy) on the coupling component.
- On the diazo, substituents increase fastness in order of meta < para < ortho

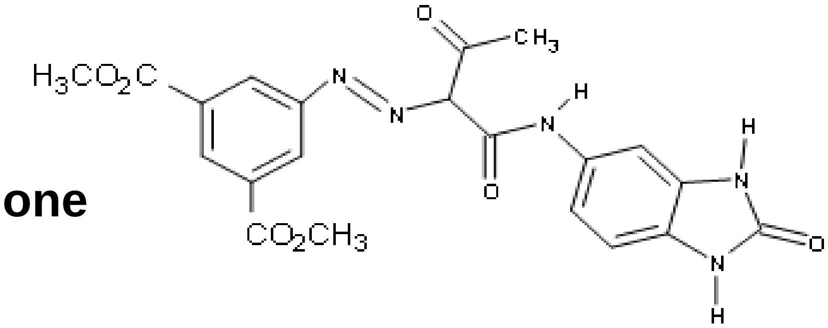
PR15
Naphthol AS



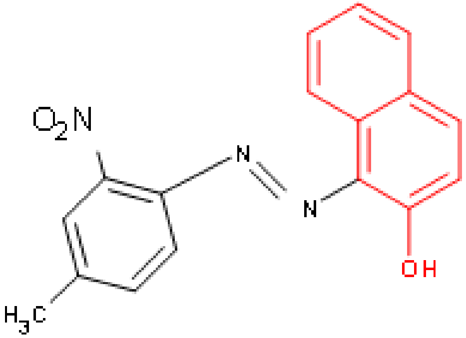
Fastness Properties

- Substituents such as alkyl, alkoxy, alkylamino or sulfonic acid increase solubility.
- Carbonamide, nitro and chloro groups are insolubilizing substitutents.
- Pigment lakes are usually fast to organic solvents.
- Increasing molecular weight usually improves solvent resistance.

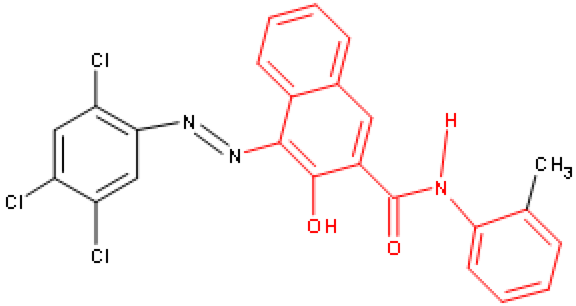
PY120
benzimidazolone



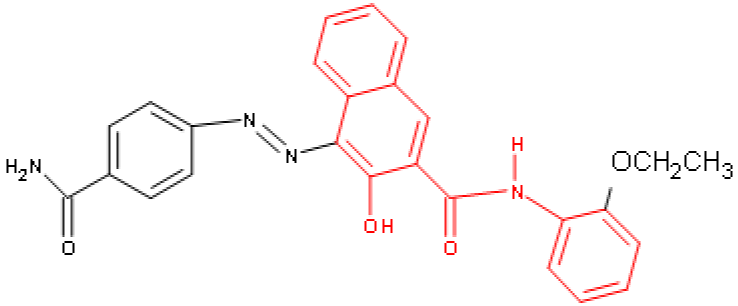
Beta Naphthol Type pigments
Non-metallized azo reds



β-naphthol
PR3, Toluidine Red

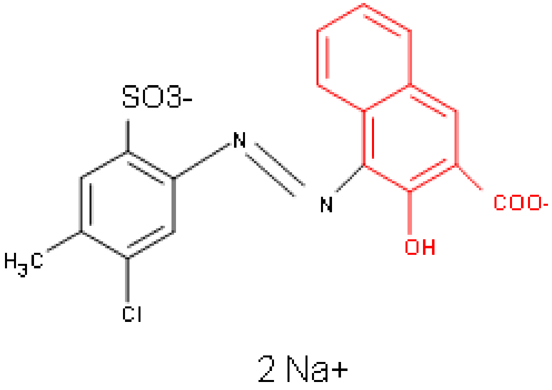


Naphthol AS pigment, Group I
PR112



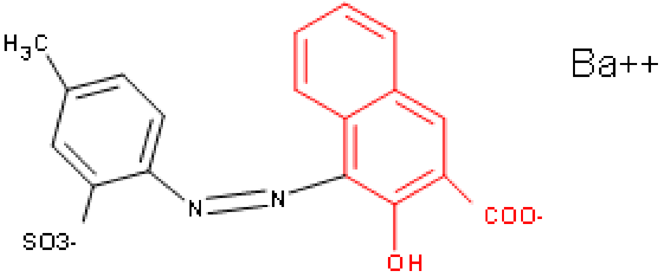
Naphthol AS pigment, Group II
PR170

Beta Naphthol Type pigments, cont.



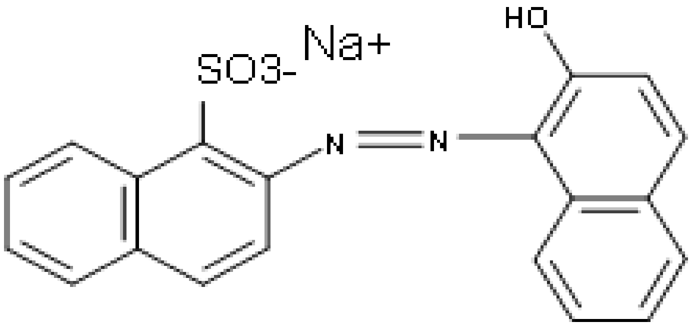
PR48
Permanent Red 2B

BONA pigments, **b**eta **o**xy **n**aphthoic **a**cid



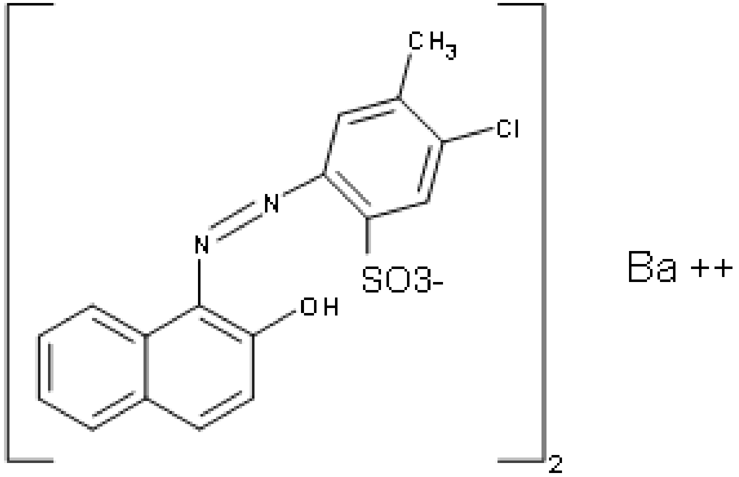
PR57:2

Beta Naphthol Type Pigments, cont., other Beta naphthol salts



PR49, Lithol Red

Pigment	Cation	Hue
PR49	Na	Yellowish red
PR49:1	Ba	Bluish pink
PR49:2	Ca	Bluish pink
PR49:3	Sr	Bluish red

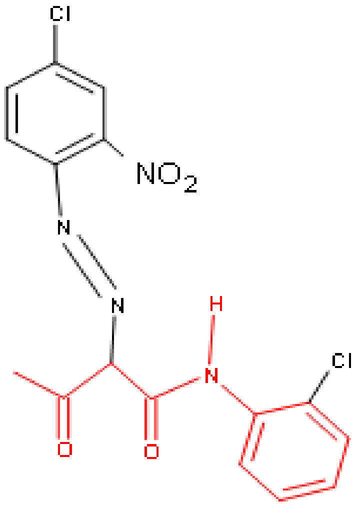


PR53:1
Red Lake C

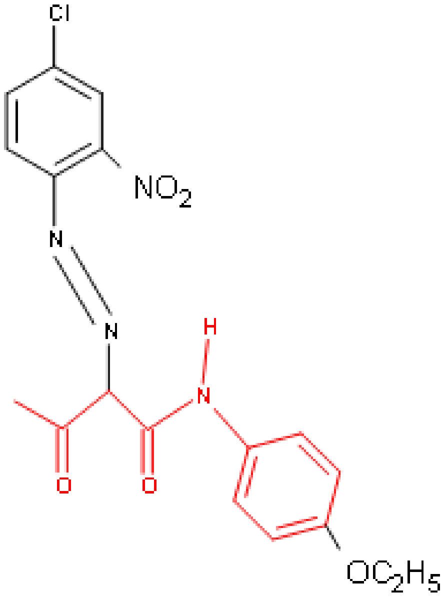
Monoarylide Yellows

- Often called Hansa yellows or arylide yellows
- Uses acetacetarylide (acetarylamide) as coupling components
- PY1 patented in 1909 as Hansa Yellow G
- Characterized by poor solventfastness
- Fairly good lightfastness

PY3

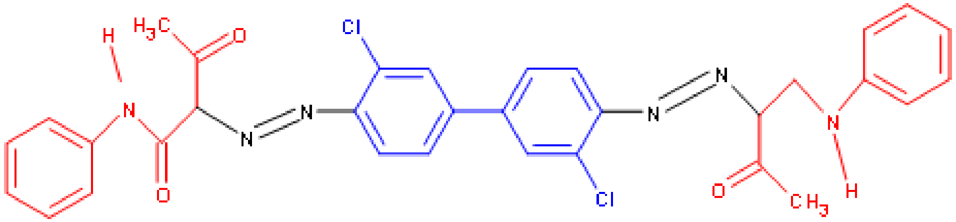


PY75

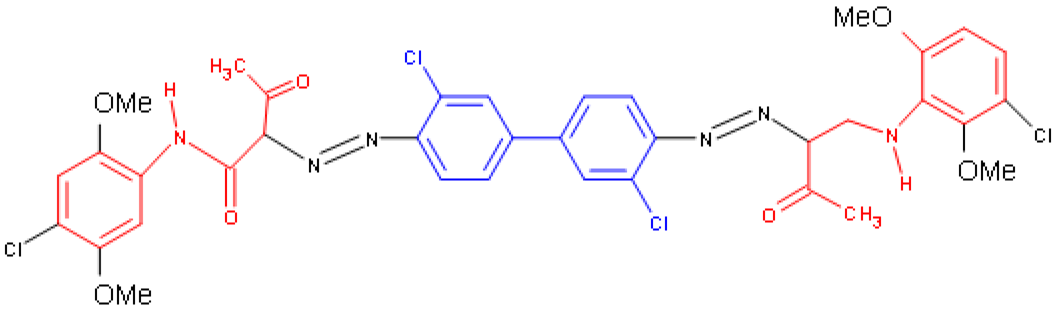


Diarylide Yellows

- 3,3’ dichlorobenzidine backbone
- Higher tinting strength than monoarylide yellows
- Better solvent fastness
- Poor lightfastness
- Used extensively in the printing ink industry



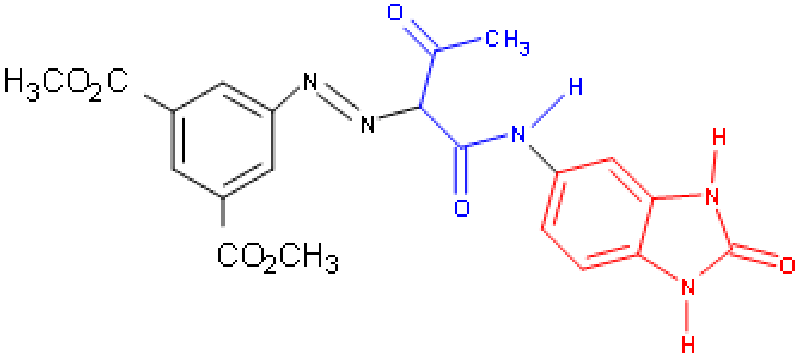
PY12



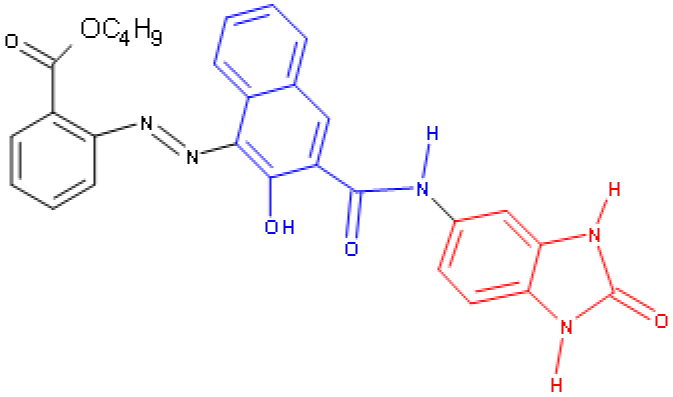
PY83

Benzimidazolones

- First patent applied for in 1960
- Introduced to improve fastness properties
- Two main structures—
  - Arylide yellow type
  - Naphthol AS type
- Arylide yellow type are yellow and orange
- Naphthol AS type are red, violet and brown



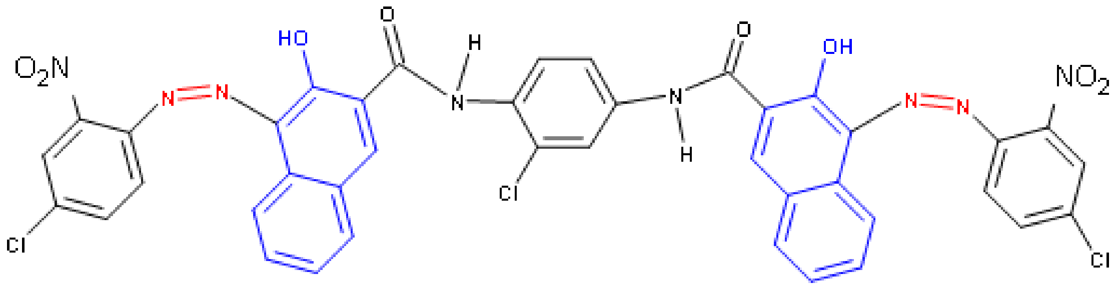
PY120



PR208

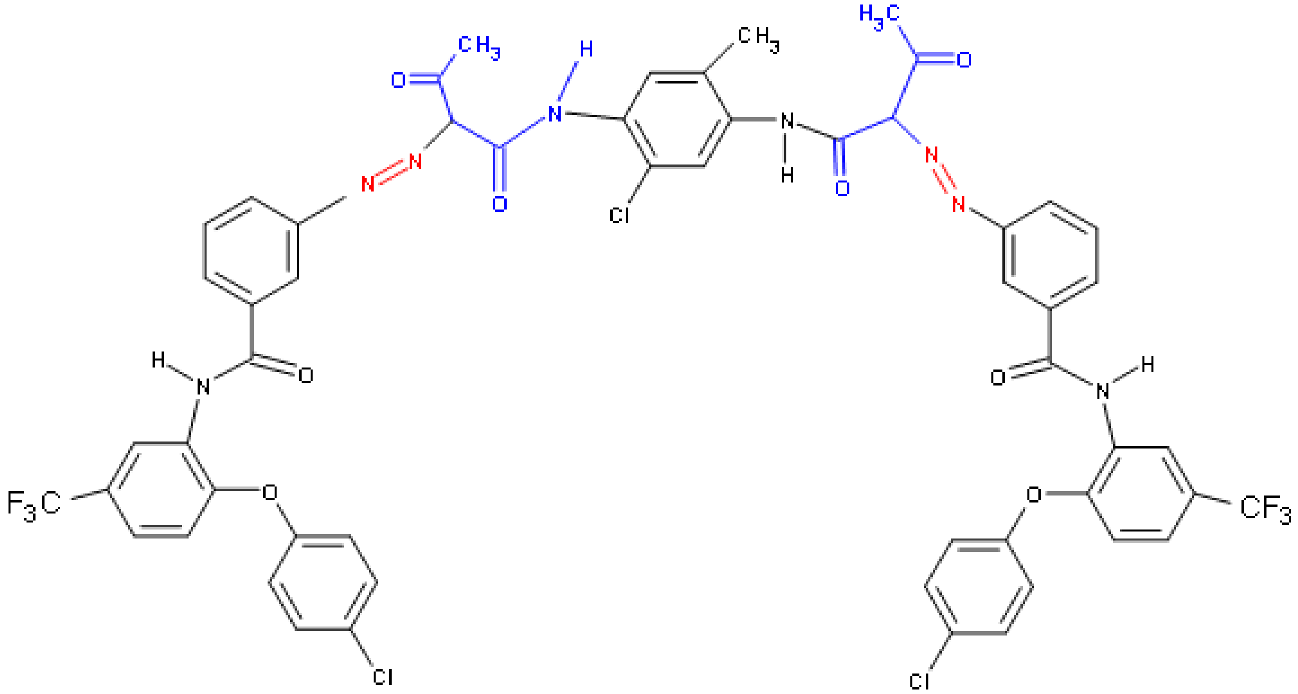
Disazo Condensation Pigments

- Made to confer solvent resistance
- First synthesized in the early 1950s
- Formed from two monoazo units
- There is a yellow series & an orange, red and brown series



PrBr23

Disazo Condensation Pigments

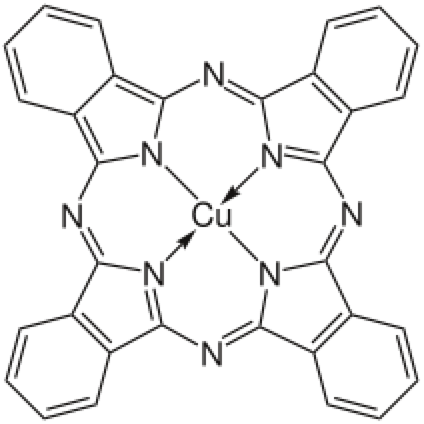


PY128

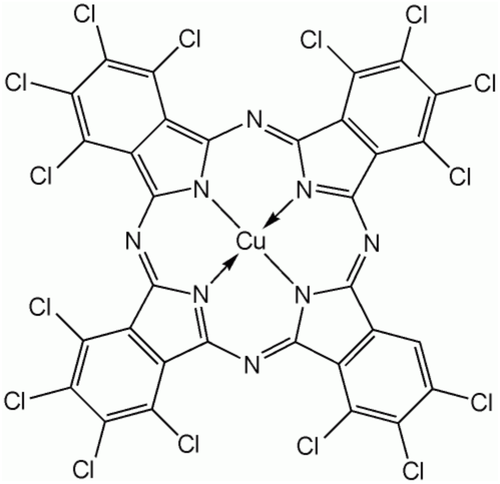
Phthalocyanine

- Blues marketed as early as 1935, greens in 1940.
- Blues exist in 2 crystalline forms and can be stabilized
- Halogenation gives greens
- Excellent fastness properties

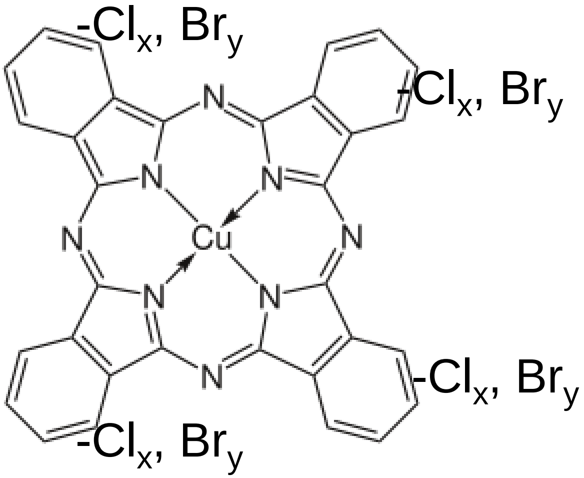
PB15, phthalocyanine blue



PG 7, blue shade green

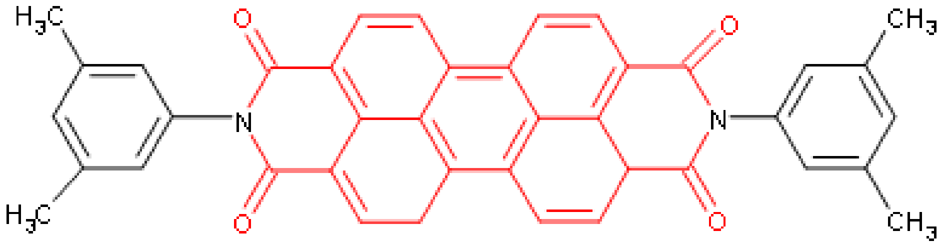


PG 36, yellow shade green

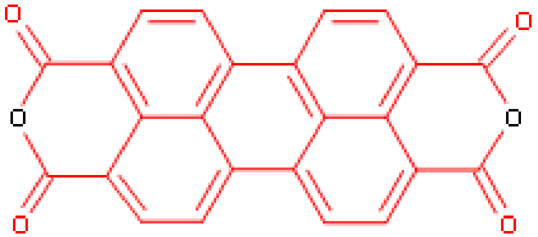


Perylenes

- First introduced in the late 1950s
- Excellent fastness properties



PR149

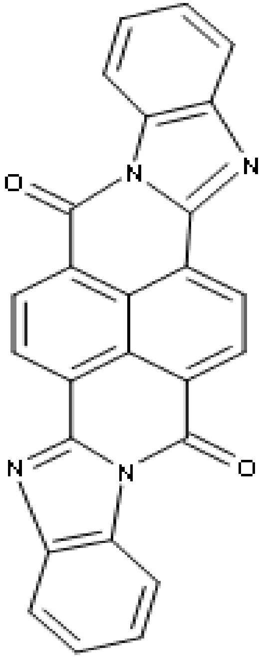


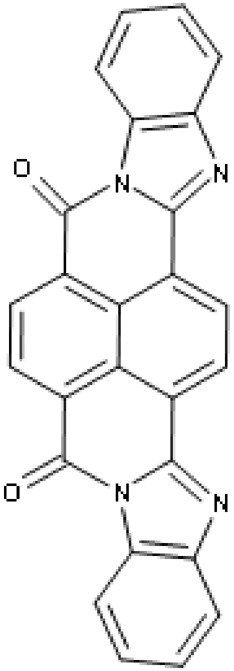
PR224

Perinones

- Reaction discovered in 1924 but not introduced as pigments until the 1950s
- Two major members of this class

PO43

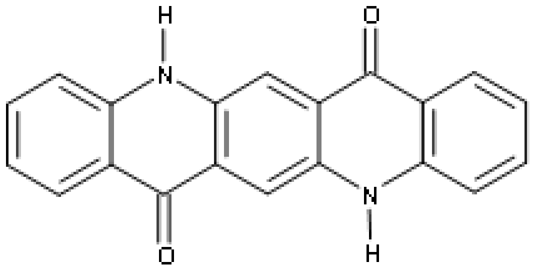




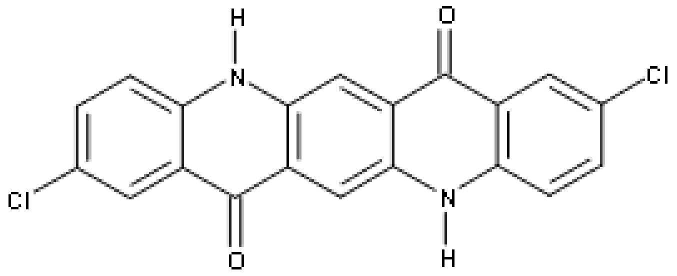
PR194

Quinacridones

- First synthesized in 1935
- Not introduced as pigments until the 1950s
- The parent linear trans quinacridone exists in 4 crystalline phases
- Substitution changes the color of the pigment



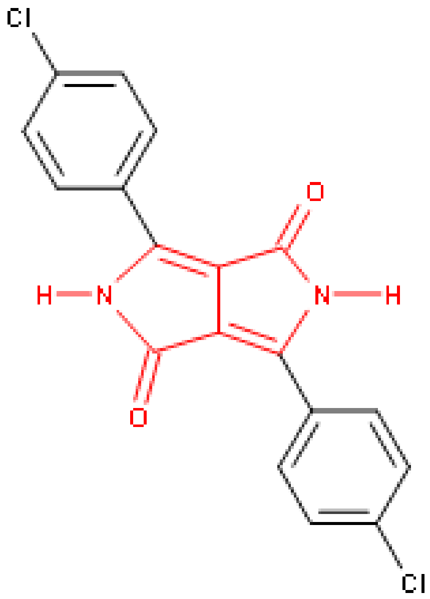
PV19
red violet to
bluish red



PR202
bluish red to
violet

DPP pigments

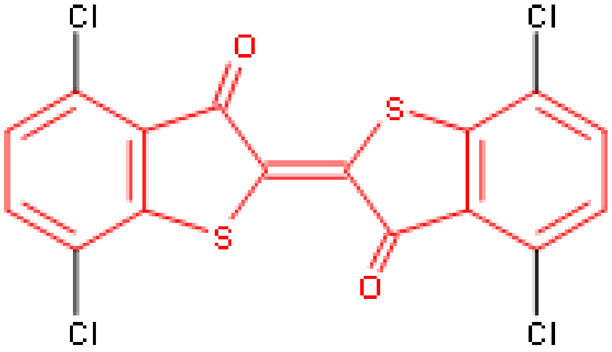
- Diketopyrrolopyrrole
- Synthesized by Ciba Geigy in the 1980s
- Range in color from reddish yellow to bluish violet
- Excellent fastness properties



PR254

Thioindigo pigments

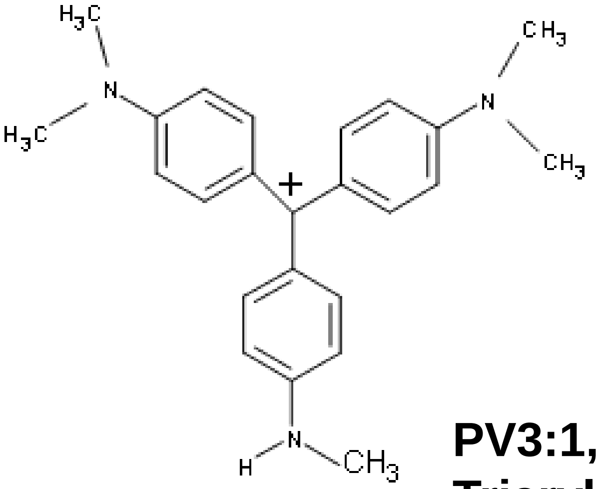
- Good fastness properties
- Used in automotive finishes
- Discovered in 1907, but not commercialized until the 1940s



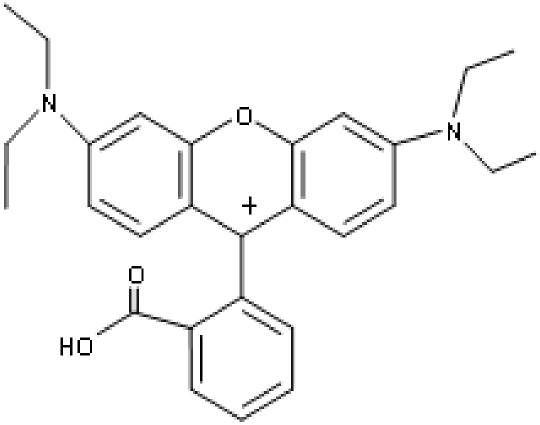
PR88

Triarylcarbonium ion and Rhodamine type pigments

- Triaryl carbonium ion first synthesized in 1913 by BASF
- Some have complex anions
  - Phosphomolybdic acid
  - Phosphotungstomolybdic acid
  - Copper ferrocyanides
  - Silicomolybdic acid

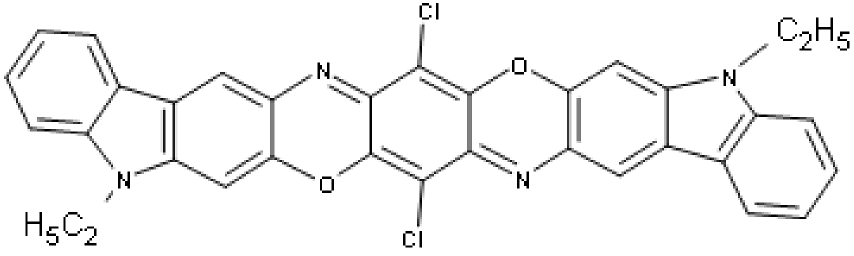


PV3:1, Triarylcarbonium Ion type

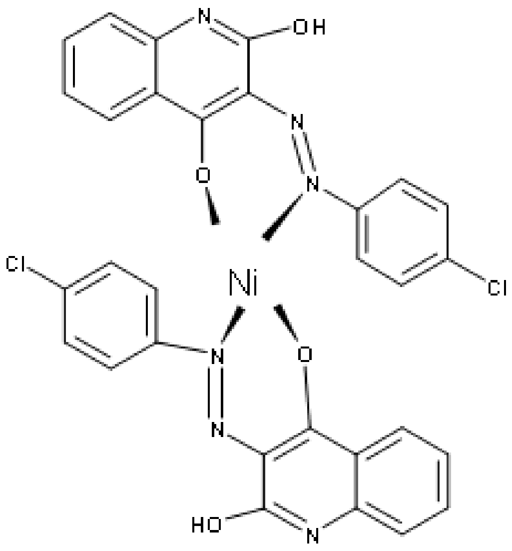


PV1, Rhodamine type

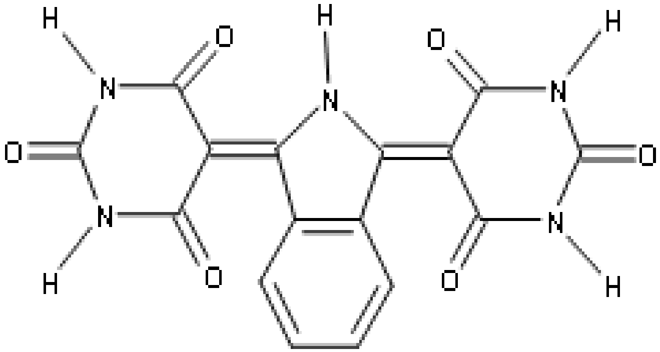
Misc. pigments



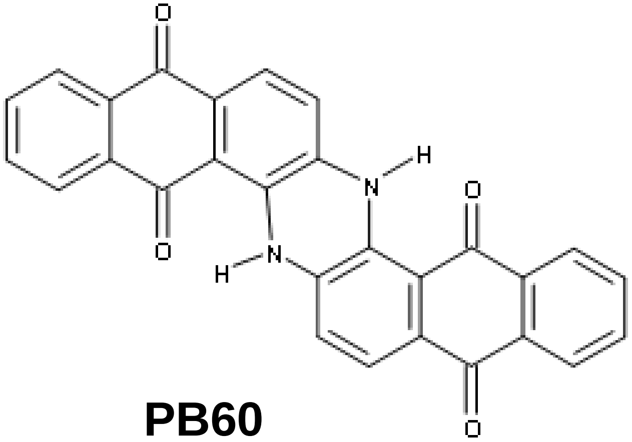
PV23



PG10



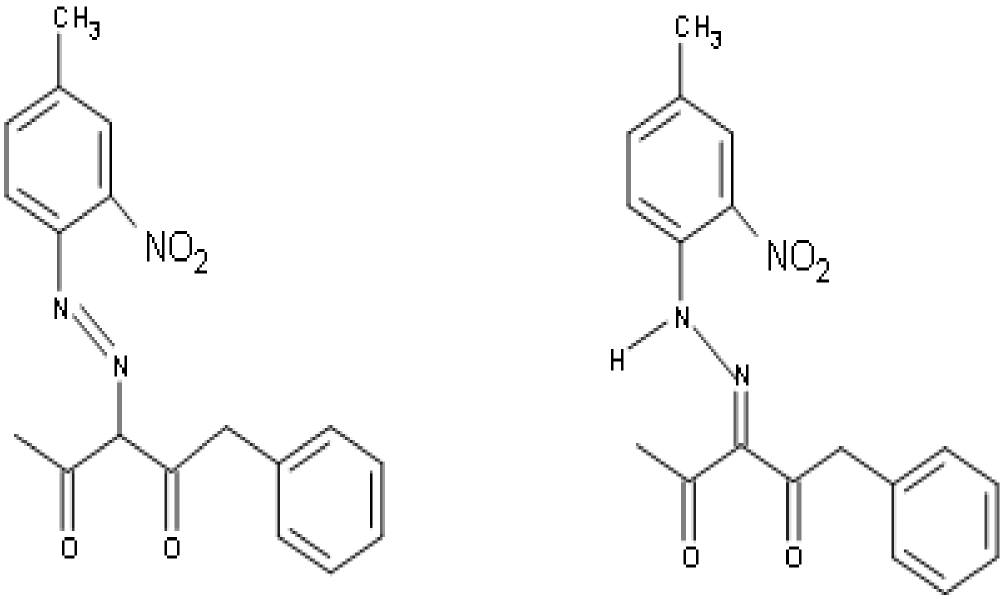
PY139



PB60

Azo to hydrazone tautomerization

- Interconverting isomers
- Usually by migration of a hydrogen atom



Resources

- Herbst and Hunger, “Industrial Organic Pigments: Production, Properties, Applications”, Wiley VCH, 2004.
- Faulkner and Schwartz, “High Performance Pigments”, Wiley VCH, 2009
- Lewis, “Organic Pigments”, Federation Series on Coating Technology, 1995
- Lomax and Learner, A Review of the Classes, Structures and Methods of Analysis of Synthetic Organic Pigments”, JAIC, 45, 107-125, 2006.
- s-lomax@nga.gov

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman analysis of 19th & 20th century synthetic organic colorants

Nadim Scherrer

Bern University of the Arts, CH

FRIDAY, SEPTEMBER 28: LECTURE 2

Bern University of Applied Sciences
Bern University of the Arts

SIK ISEA
Schweizerisches Institut für Kunstwissenschaft
Institut suisse pour l'étude de l'art
Istituto svizzero di studi d'arte
Swiss Institute for Art Research

Raman analysis of 19th and 20th C. synthetic organic colorants on artwork

by

Dr Nadim C. Scherrer, *Bern University of the Arts*

IRUG Raman Spectroscopy Workshop, September 27-28, 2012

Philadelphia Museum of Art

Infrared and Raman Users Group

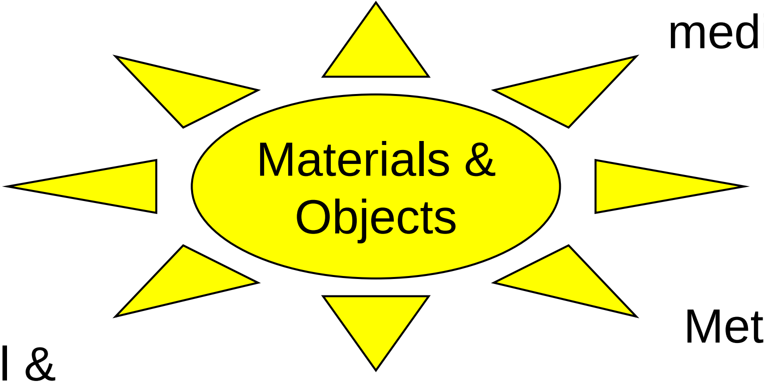
A collaboration to encourage the exchange of information, develop IR and Raman spectral standards, and distribute comparative spectral data for the study of works of art, architecture, and archeological materials.

PHILADELPHIA MUSEUM OF ART

Outline

1. **Definition** of materials analysed with Raman
2. Explanation on the kind of **information gained by Raman**
3. Typical **instrument setup** used
4. **Sample requirements**
5. **Problems encountered** and possible solutions
6. **Spectral interpretation** on synthetic organic pigments
7. Case Studies
8. **Advantages and limitations** of Raman with organic pigments
9. Summary
10. Reference papers

Range of painted or coloured materials coming through the lab...



Materials & Objects

Paintings & sculptures

Architecture, furnishing & furniture

Modern materials & media

Books, graphics & photographic objects

Textiles, fabrics

Archeological & ethnographic objects

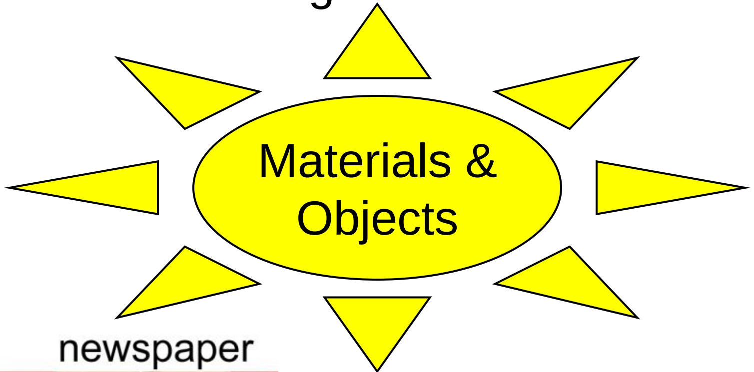
Metal & glass

Technical & scientific instruments

Paintings

Bernese sledge

Citroen Mehari



Materials & Objects

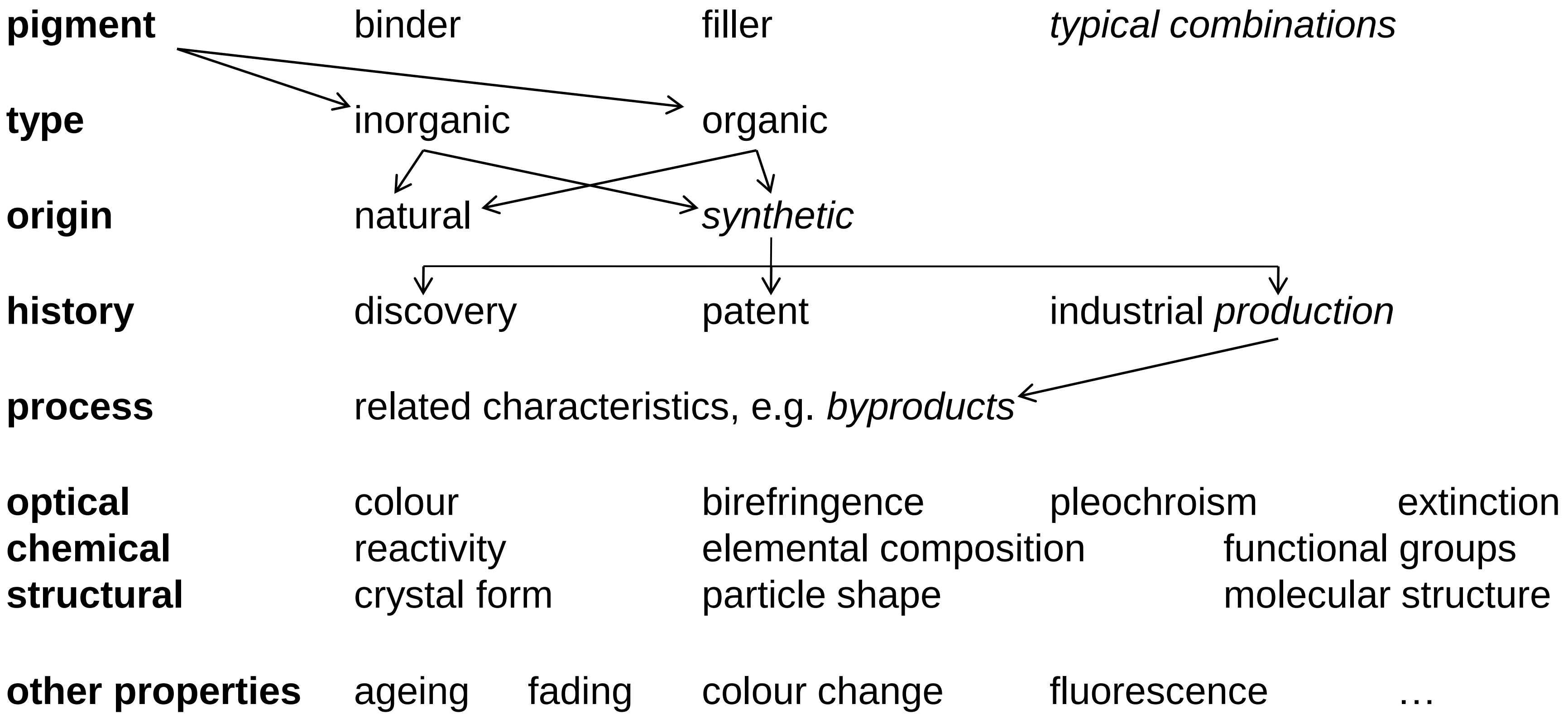
Textiles

12th C. bookcover

Model train “Krokodil”

Organising pigment analysis…

paint is not just pigment… and there is potential to track down the history of a paint layer…



pigment binder filler *typical combinations*

type inorganic organic

origin natural *synthetic*

history discovery patent industrial *production*

process related characteristics, e.g. *byproducts*

optical colour birefringence pleochroism extinction
chemical reactivity elemental composition functional groups
structural crystal form particle shape molecular structure

other properties ageing fading colour change fluorescence …

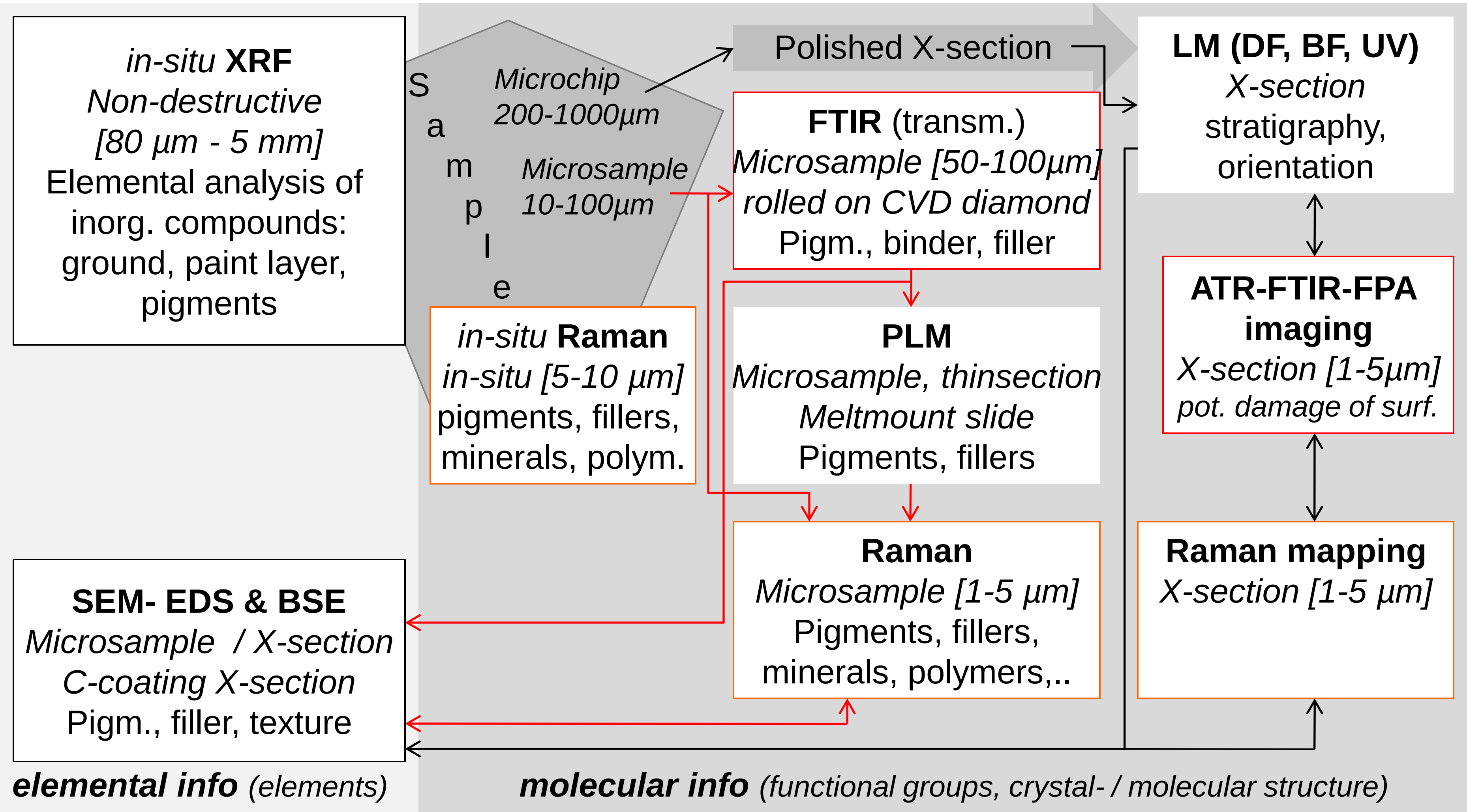
Technical constraints and their relevance…

… the hypermachine doesn't exist yet, there is still potential for development…!

sampling	minimal invasion	selective	original material				
preparation	in-situ	sectioning	coating	rolling	dissolution	grinding	separation
excitation	type/wavelength	penetration	artefacts (heating, diffusion,…)				
spatial res.	spot size	penetration depth	*interaction volume*				
spectral res.	interference	time of analysis	*no. of spots over range covered*				
spec. range	coverage	*filter cut off*	*detector efficiency*				
detection	limit	S/N ratio	saturation				
information	elemental	molecular	optical	surface	1D/2D/3D		
concentration	sample size	spot size	integration time				
visual control	orientation	spot/line/image selection	*context information*				

HKB Lab: analytical instruments for elemental and molecular characterisation of materials, e.g. paintlayers.

General requirements: no (in-situ) or minimal sample use (microsamples)



in-situ **XRF**
Non-destructive
[80 µm - 5 mm]
Elemental analysis of inorg. compounds: ground, paint layer, pigments

Sample

Microchip 200-1000µm

Microsample 10-100µm

Polished X-section

LM (DF, BF, UV)
X-section
stratigraphy, orientation

FTIR (transm.)
Microsample [50-100µm] rolled on CVD diamond
Pigm., binder, filler

in-situ **Raman**
in-situ [5-10 µm]
pigments, fillers, minerals, polym.

PLM
Microsample, thinsection
Meltmount slide
Pigments, fillers

ATR-FTIR-FPA imaging
X-section [1-5µm]
pot. damage of surf.

SEM- EDS & BSE
Microsample / X-section
C-coating X-section
Pigm., filler, texture

Raman
Microsample [1-5 µm]
Pigments, fillers, minerals, polymers,..

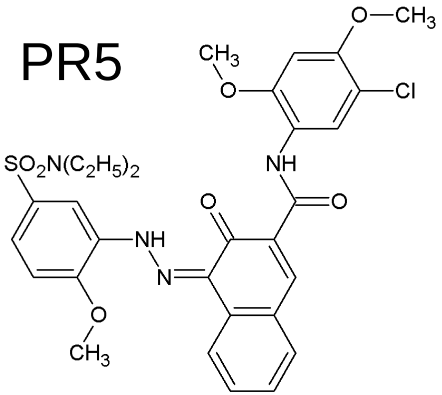
Raman mapping
X-section [1-5 µm]

elemental info *(elements)*

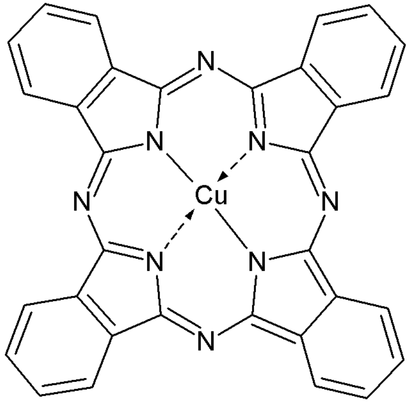
molecular info *(functional groups, crystal- / molecular structure)*

1 Definition of materials analysed with Raman

PR5



PB15



With respect to the chemical structure and properties of synthetic organic pigments, you are referred to the previous presentation by Suzanne Lomax, she is an expert on it – whereas my background is somewhat more inorganic…

- **Synthetic organic pigments** consist of molecules with **functional groups** combined from **C, N, H and O** – in some cases combined or **complexed** with metals, such as e.g. **Cu, Ni, Cr, Fe, Co**
- **Lakes** are organic dyes often precipitated on a metallic salt as a **substrate** such as e.g. **CaCO3** [calcite], **BaSO4** [baryte], **AlSO4** [aluminiumsulfate], KAl(SO4)2 [alum], Al2O3 [synthetic corundum or alumina] or organic substrates such as starch.

1 Definition of materials analysed with Raman

- History of synthetic dyes begins with discovery of mauve in 1856
- Discovery of disazo compounds in 1861
- Enormous expansion of organic pigment development in early 20th C.
- Looking at the composition of current artist's paint products (2008), synthetic organic pigments are well established and may occur as single pigment paints or may be combined with up to 5 different organic and/or inorganic pigments
- Such multi-pigment paints are definitely more challenging to interpret

1 Definition of materials analysed with Raman

In 2008, we looked at **16 different product lines** from Schmincke, Talens, Winsor&Newton, Golden Acrylics and counted **120 different pigments** of which **71 were of synthetic organic** and **49 of inorganic** nature

This table set the basis for our synthetic organic pigment reference collection that now comprises a total of **174 C.I. numbers** and **235 products**.

One question we were interested in was the potential to **distinguish the same pigment from different sources or batches and dates?** – The answer was no, not with Raman. The only distinctive observation was that for the 8 samples of **PY3** we had, the two **historic** ones had a higher and **curved background**.

1 *Timeline of synthetic organic pigments with known year of introduction or discovery, listed in those 16 paint products* (Scherrer et al. 2009)

Discovery	First Prod.		C.I. Name	C.I. Number	C.I. Category	Pigment Group
1826		🟥	**PR83**	58000	Anthraquinone	Anthraquinone
1826		🟥	**PR83:1**	58000:1	Anthraquinone	Anthraquinone, Ca
1903		🟥	**PR57**	15850	Monoazo	BON lake
1903		🟥	**PR57:1**	15858:1	Monoazo	BON lake, Ca
1907	1908	🟧	**PO5**	12075	Monoazo	B-Naphthol
1910	1910	🟨	**PY3**	11710	Monoazo	Acetoacetic arylide
1911		🟥	**PR23**	12355	Monoazo	Naphthol AS
1913		🟥	**PR179**	71130	Anthraquinone	Perylene
1921		🟩	**PG8**	10006	Nitroso	Nickel complex, Fe acid dye
1921		🟥	**PR9**	12460	Monoazo	Naphthol AS
1921		🟥	**PR12**	12385	Monoazo	Naphthol AS
1901	1924	🟦	**PB60**	69800	Anthraquinone	Indanthrone
1907	1928	🟦	**PB15**	74160	Phthalocyanine	Phthaloblue Cu, not stable
1907	1928	🟦	**PB15:1**	74160:1	Phthalocyanine	Phthaloblue Cu, a-mod.
1907	1928	🟦	**PB15:2**	74160:2	Phthalocyanine	Phthaloblue Cu, a-mod.
1931		🟥	**PR5**	12490	Monoazo	Naphthol AS
1935	1936	🟩	**PG7**	74260	Phthalocyanine	Phthalogreen Cu
1931	1939	🟦	**PB16**	74100	Phthalocyanine	Phthaloblue, metal free
1939		🟥	**PR112**	12370	Monoazo	Naphthol AS

1 *Timeline continued…*

Discovery	First Prod.		C.I. Name	C.I. Number	C.I. Category	Pigment Group
	1953	🟩	**PB15:3**	74160:3	Phthalocyanine	Phthaloblue Cu, B-mod.
1928	1953	🟪	**PV23**	51319	Oxazine	Dioxazine
1956		🟥	**PR149**	71137	Anthraquinone	Perylene
1957		🟨	**PY73**	11738	Monoazo	Acetoacetic arylide
	1958	🟨	**PY83**	21108	Disazo	Diarylide
1935	1958	🟥	**PR122**	73915	Indigoid	Quinacridone
1935	1958	🟪	**PV19**	73900	Indigoid	Quinacridone
1957	1959	🟩	**PG36**	74265	Phthalocyanine	Phthalogreen Cu
1956	1961	🟨	**PY109**	56284	Aminoketone	Isoindolinone
1958	1961	🟨	**PY74**	11741	Monoazo	Acetoacetic arylide
1961	1961	🟨	**PY97**	11767	Monoazo	Acetoacetic arylide
1956	1965	🟨	**PY110**	56280	Aminoketone	Isoindolinone
1960	1966	🟫	**PBr25**	12510	Monoazo	Benzimidazolone
1974		🟥	**PR254**	56110	Aminoketone	Diketopyrrolo-Pyrrole (DPP)
1983		🟥	**PR255**	561050	Aminoketone	Diketopyrrolo-Pyrrole (DPP)
1983		🟥	**PR264**	561300	Aminoketone	Diketopyrrolo-Pyrrole (DPP)
	1975	🟨	**PY154**	11781	Monoazo	Benzimidazolone

2 Kind of information delivered by Raman

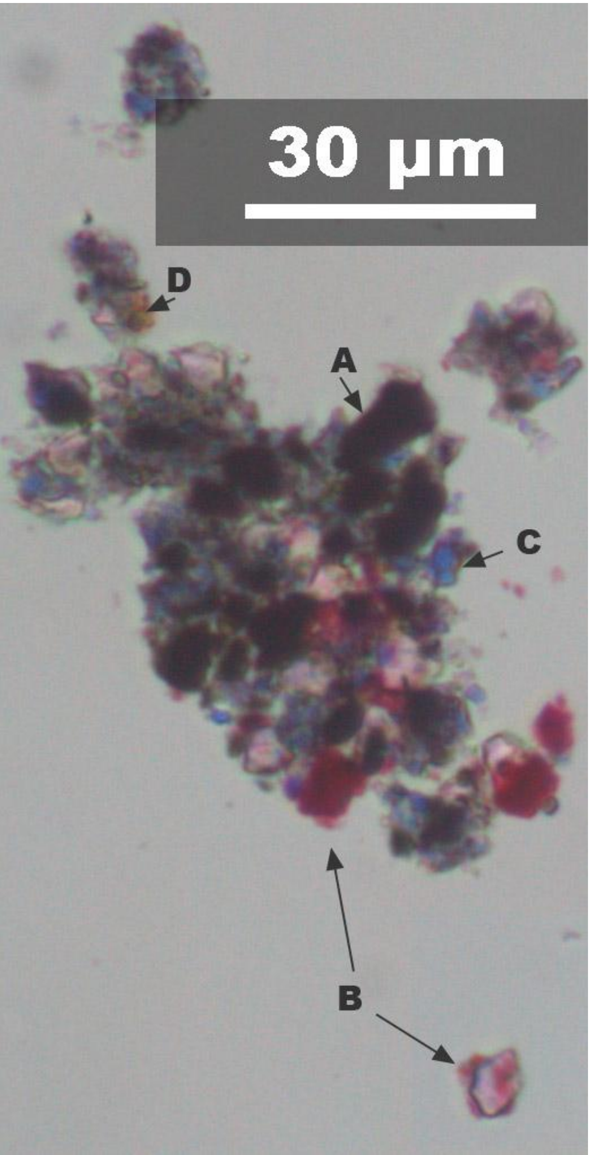
Raman analysis **can be time consuming** and since there is no standard setting like with FTIR or SEM-EDS analyses, it is not always the most efficient technique for routine paint analysis.

For this reason Raman comes into action for **specific questions** rather than routine analysis and thus is a **complementary** technique

e.g. **Authentication**:

- Check for organic pigments e.g. if
  - µ-XRF did not deliver color-specific elements
  - FTIR suggests the presence of organic pigments
  - Paint sample is still soft…
  - Distinction of TiO2 **polymorphs** (chronology)
  - Check for **pigment mixtures** (synth. organic besides inorganic)

2 *Strength of Raman analysis*



Raman has specific advantages over FTIR and SEM-EDS:

- It allows analysis to be performed **at depth through transparent materials**
  - i.e. reverse glass paintings
  - Covered PLM pigment slides
- **No sample preparation**, no waste of microsample
- Can be applied **before or after FTIR, SEM-EDS or PLM** as an additional/complementary technique
- Very **powerful with synthetic organic pigments**
- Generally **low contribution of binding media** at 785nm excitation
- **Ease of interpretation** with a good reference database
- **High spatial resolution** allowing to target single pigment particles
- Delivers structural information for **polymorph distinction**

2 *Contrast Raman and FTIR*

FTIR analysis on paint samples is a long established and efficient technique. There are several **strengths of FTIR** over Raman:

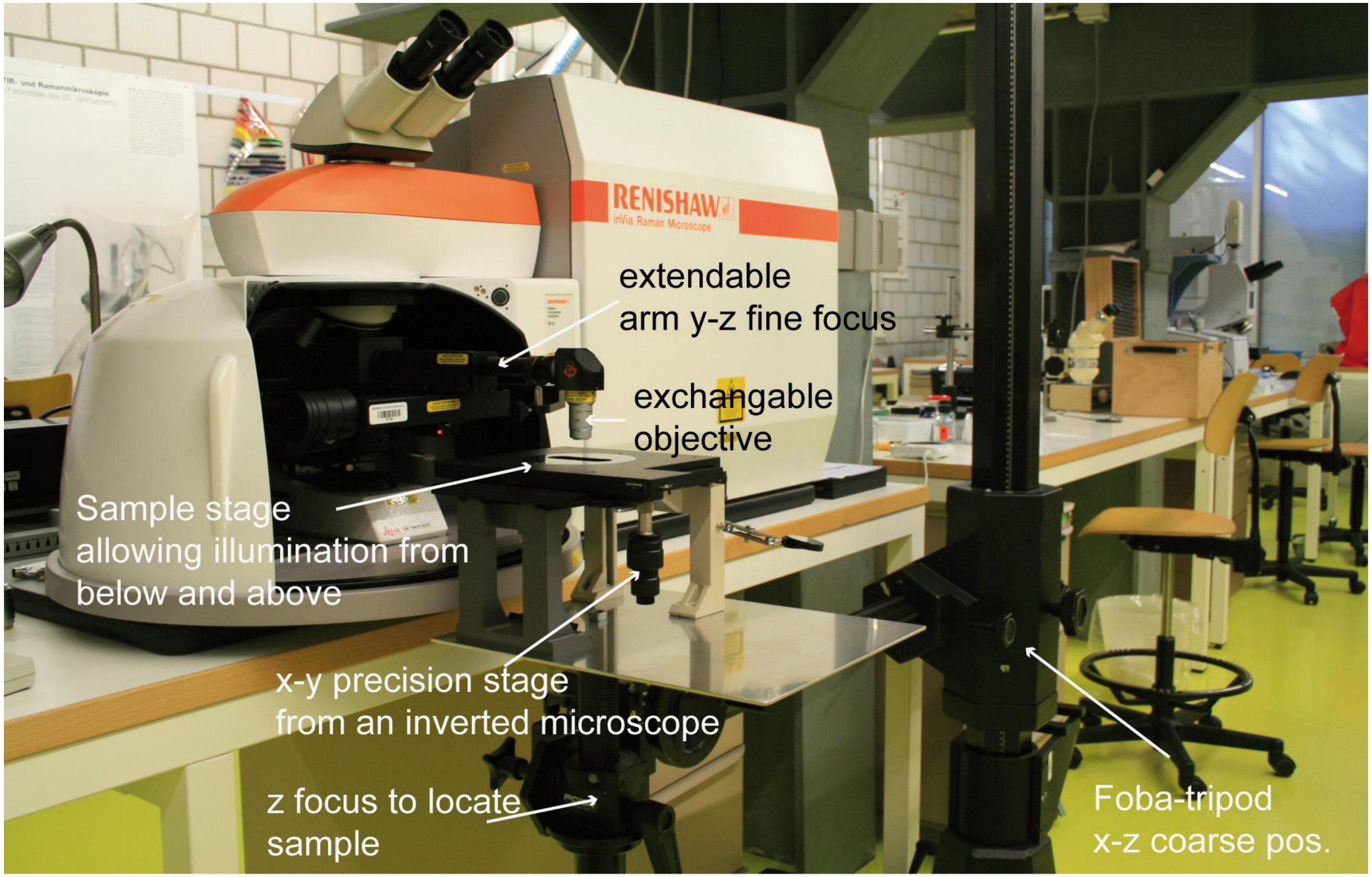
- **FTIR** generally delivers a result within seconds, i.e. **very efficient**
- There are only few factors to play with the settings (**simple** proc.)
- Generally **good response by most materials** within a paint sample with **one setting** allow for good results with FPA **imaging or mapping** experiments
- FTIR can deliver an **overview of components** with one analysis (binding media, pigment, filler), but it also may **suffer from considerable overlaps** e.g. from silicates, carbonates or soaps
- **Raman** response on **binding media is poor**, which is **ideal to identify synthetic organic pigments**
- The use of a reference database matching algorhythm works better since the response of the multiple components within the paint system is more selective
- **Raman is the technique of choice to identify organic pigments in paint**

3 Instrument setup

Renishaw InVia Reflex system (January 2007)

- **785nm** diode-laser, P_L 300 mW, P_S ~12.1mW, 1200mm/l, 120-3200cm^{-1}
- 633nm He-Ne-laser, P_L 17mW, P_S~10.3mW, 1800mm/l, 100-4000cm^{-1}
- 514nm Ar-laser, P_L 24mW, P_S~11.4mW, 1800mm/l, 100-4000cm^{-1}
- Edge filters for all 3 lasers
- 5x, 20x, **50x LWD**/NA 0.5/WD 8mm, 50x, **100x**/NA 0.9/WD 0.27mm Obj.
- Motorized x-y-z stage allowing mapping and depth profiling
- 'extendable arm' for in-situ setup outside sample chamber

3 *'Extendable arm' for in-situ analysis outside sample chamber*

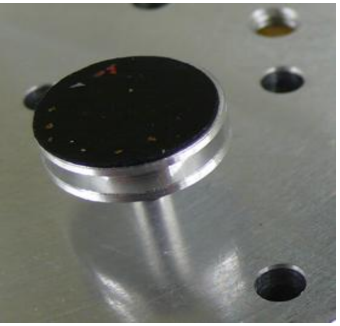


4 Sample requirements

Mostly we use **microsamples** taken with an edged tungsten needle. The gain of information with such a microsample tends to be considerably more reliable, than totally non-destructive analysis. Microsamples can be analysed sequentially with complementary techniques (FTIR, SEM-EDS, Raman, PLM). No specific preparation is performed for Raman.

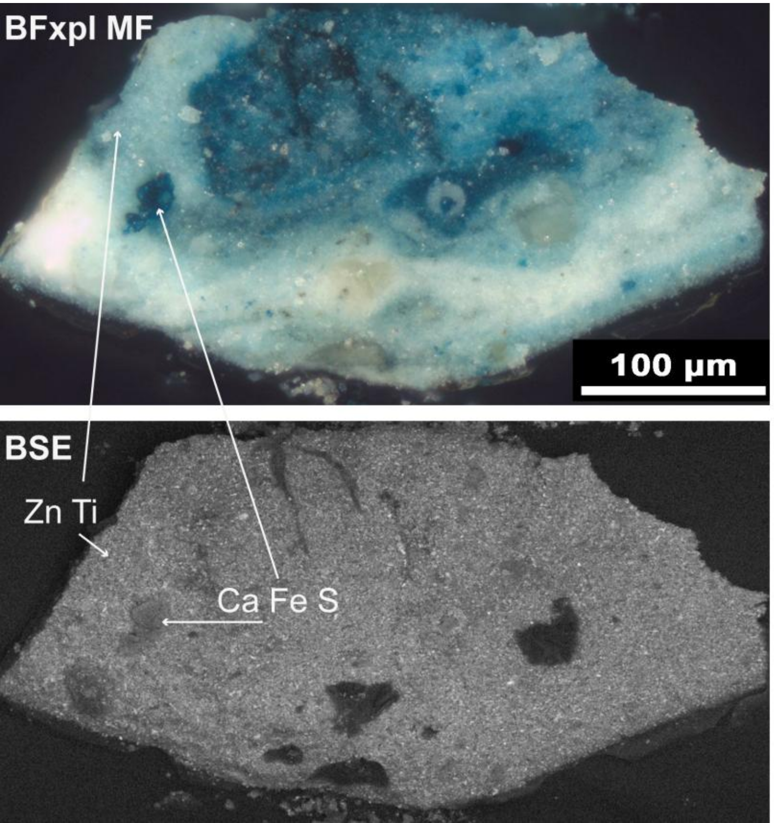
Depending on the questions and if available, we also work on dry **polished crosssections** made from embedded microsamples. On these we may sequentially apply light microscopy (LM), FTIR-FPA imaging, Raman and SEM (SE, BSE, EDS, Element mapping).

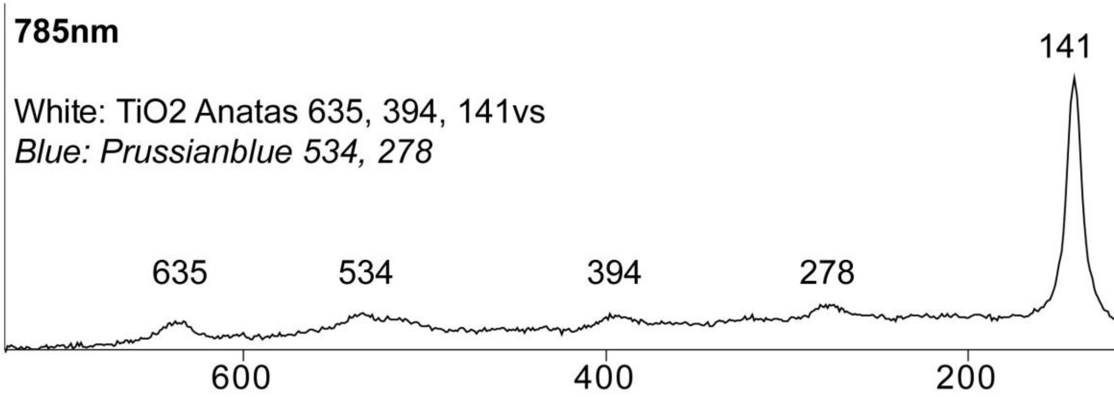
For successful Raman spot analyses on crosssections, orientation with bright field (BF) illumination can be the crux. The combination of LM images with SEM-BSE, EDS spot analyses and sometimes element maps may be of great help to locate the phases of interest to be characterized by Raman



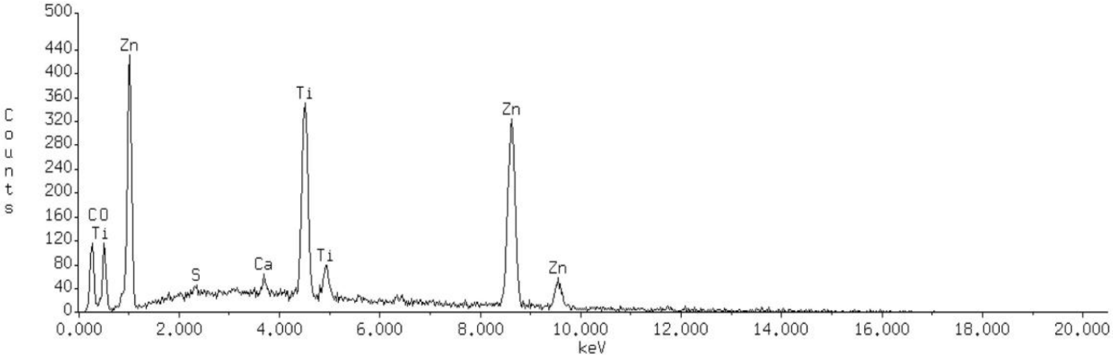
4 *Macrosample on C-tab*

- stratigraphic information without embedding
- check for presence of phthalocyanine
- identify the Ti phase

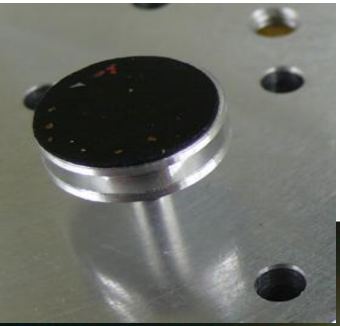


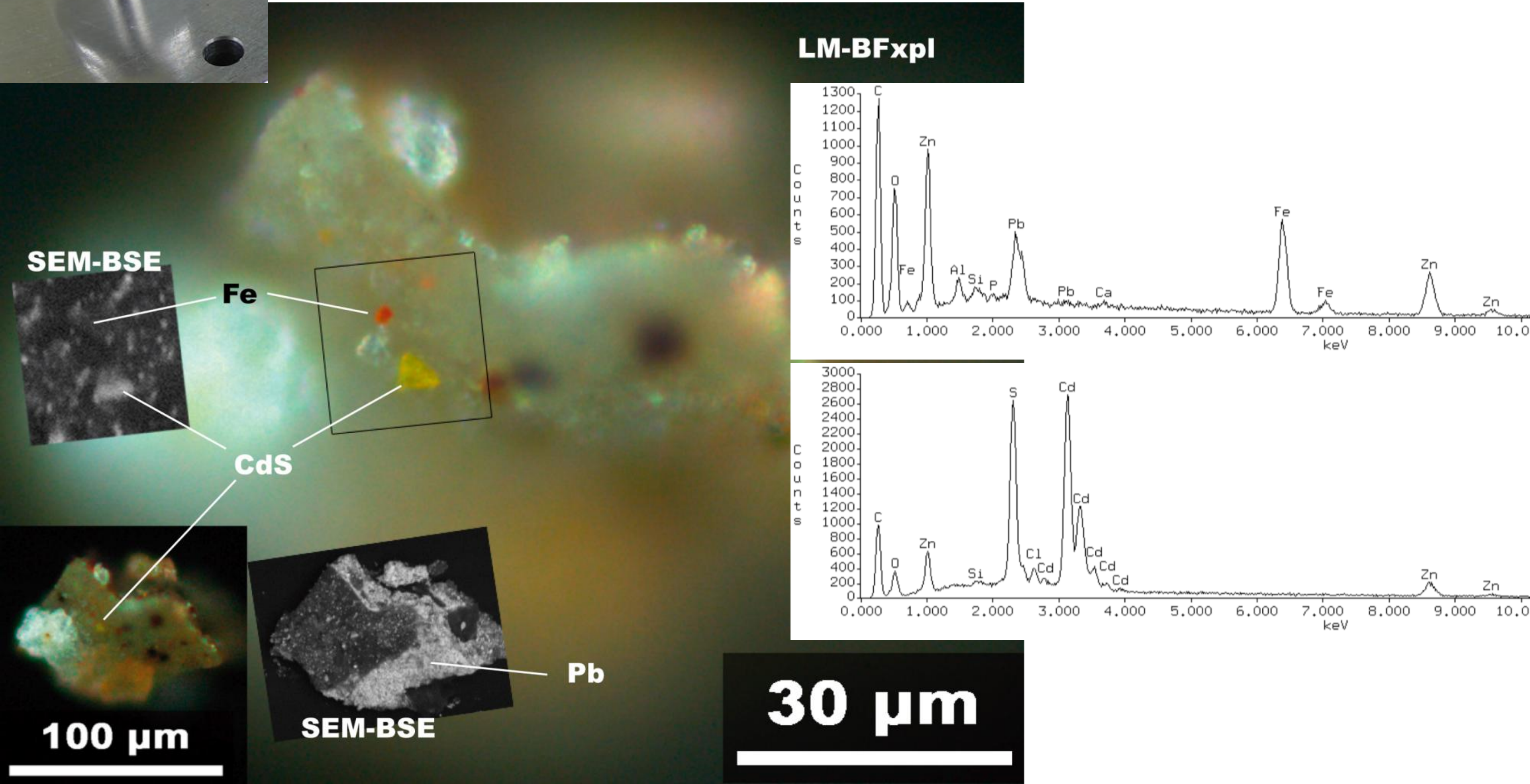

785nm

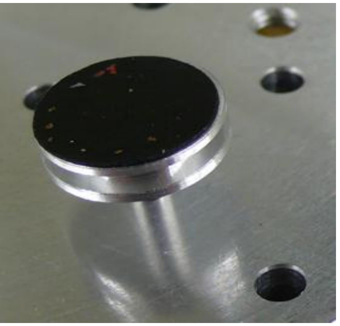
White: TiO_2 Anatas 635, 394, 141vs
Blue: Prussianblue 534, 278



4 *Microsample on C-tab*





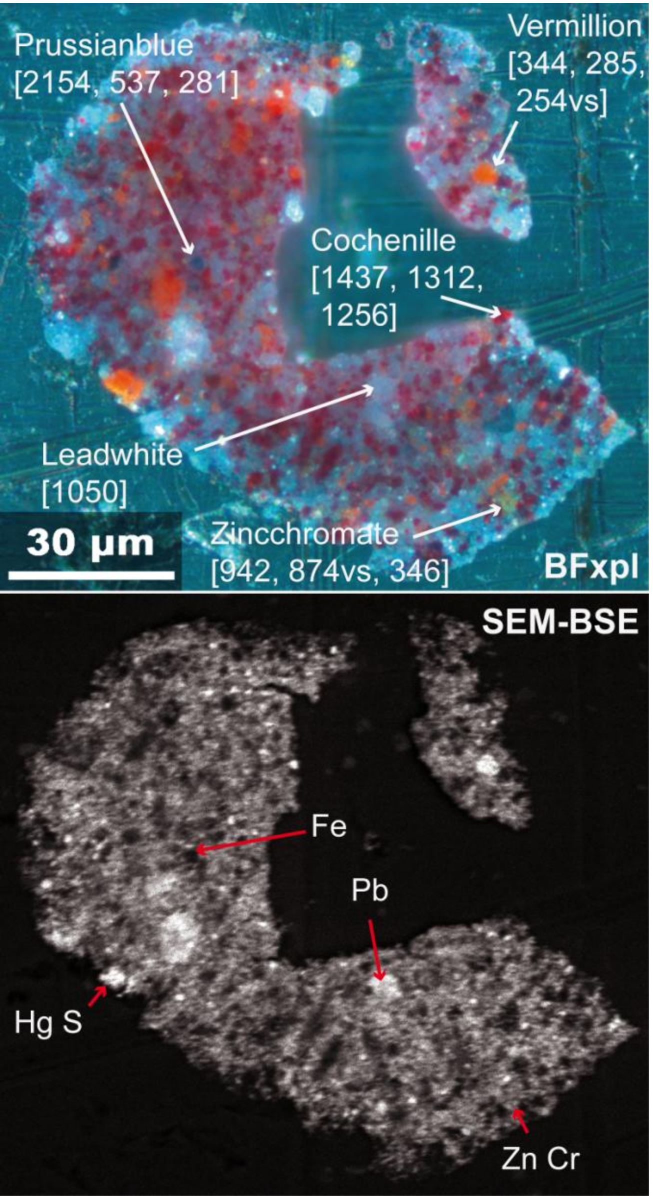


4 *Microsample on C-tab, multifocus image*

Multifocus imaging of small samples

HeliconFocus compilation of 19 focal levels

N.C. Scherrer

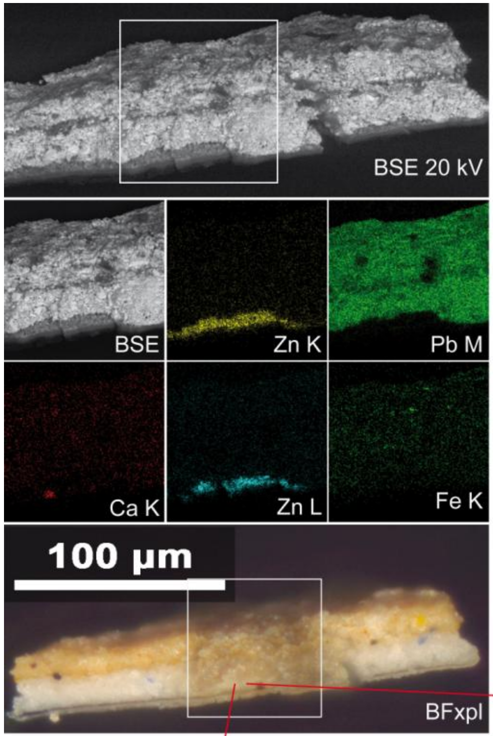


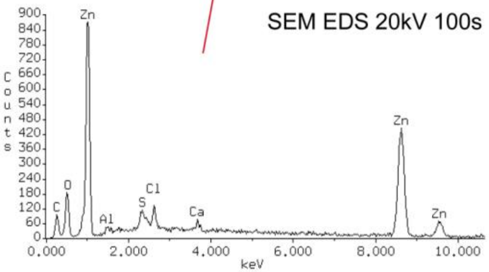
4 *Microsample rolled on Al-plate*

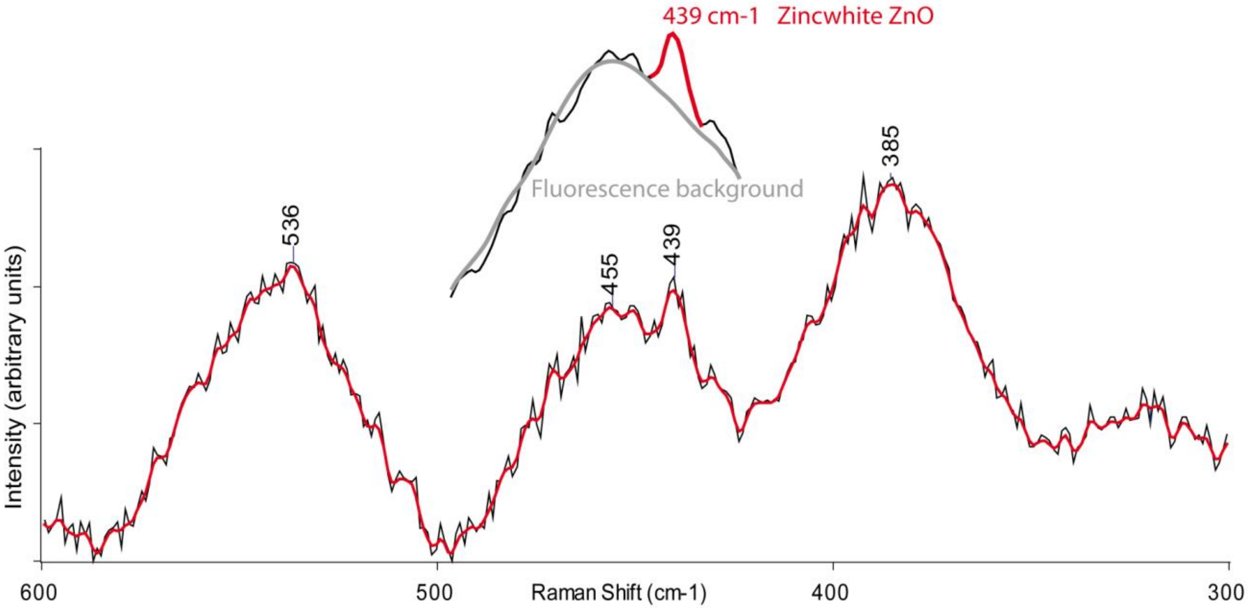
Microsamples are a cluster of particles and minor components may not always be visible or readily accessible for spot analyses, thus:

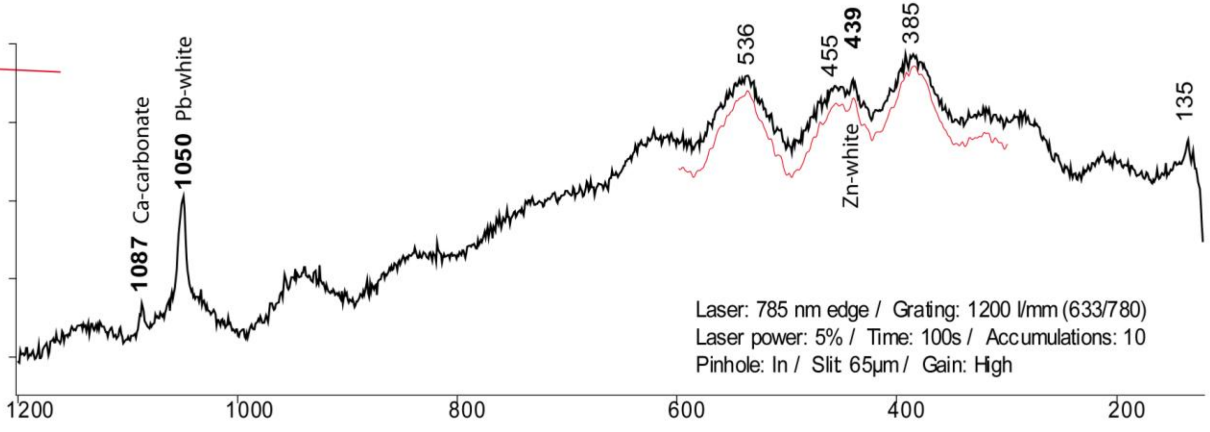
- **Rolling** the sample out with a steel roll as done for FTIR **disperses the particles** to a thin layer and makes them accessible
- LM bright field illumination with crossed polars (**BFxpl**) delivers a **perfect color contrast** to select the different particles of interest
- Using an Al-plate makes handling between LM, SEM and **Raman** easy, giving no interference (i.e. **flat background**) to the Raman analysis.
- One **disadvantage** though is the **Al** behind the thin sample in SEM-**EDS** analysis, *e.g. to solve the question on the **substrate** of the cochenille lake*

4 *Polished crosssection of microchip*





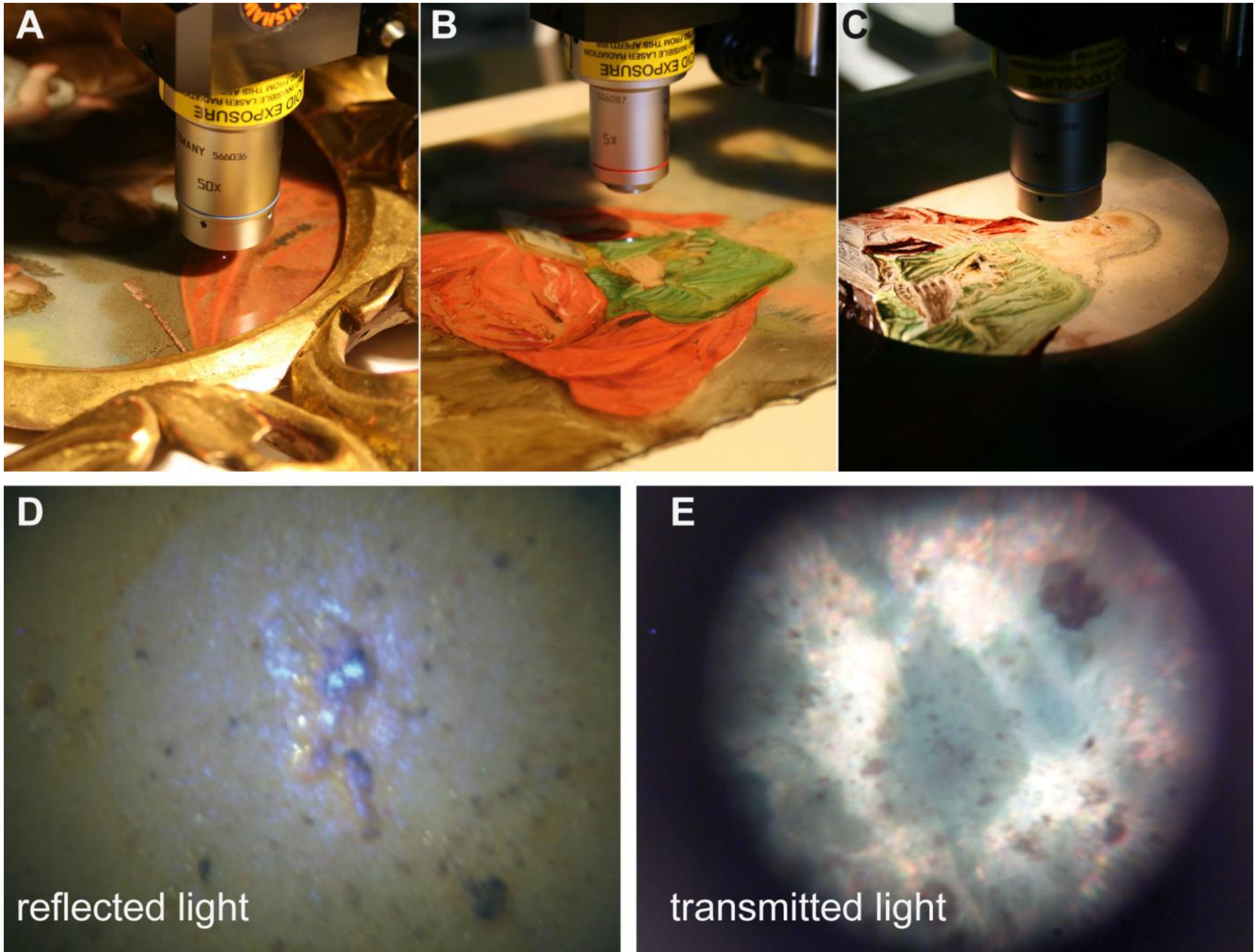




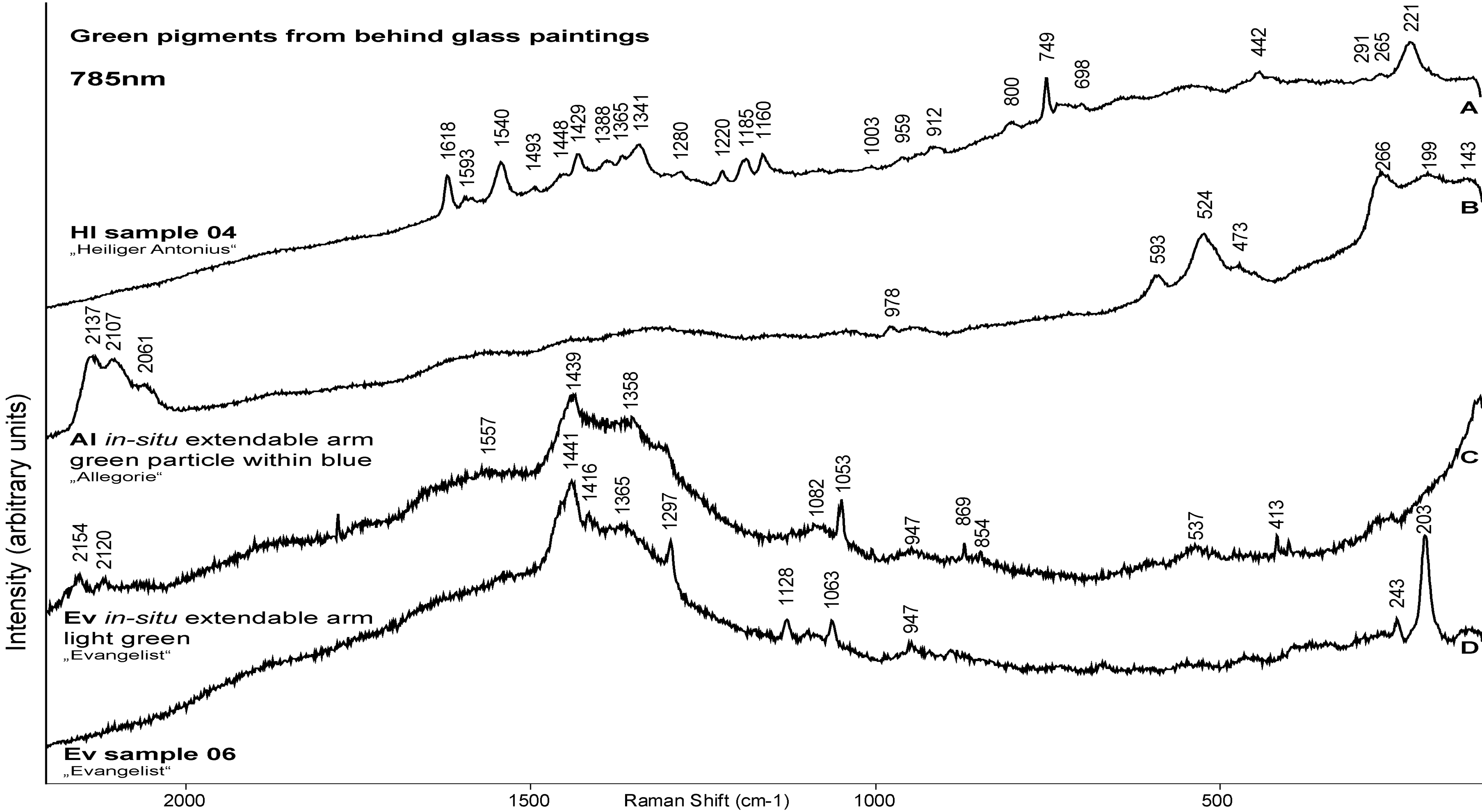
Laser: 785 nm edge / Grating: 1200 l/mm (633/780)
Laser power: 5% / Time: 100s / Accumulations: 10
Pinhole: In / Slit 65µm / Gain: High

White ground. White layer with Zn, after methanol treatment.

4 *In-situ analysis with 'extendable arm'*



4 *Comparable spectral quality with 'extendable arm'*



5 Problems encountered and possible solutions

Problem: Strongly variable intensities between sessions
  Solution: Calibration measurement on external Si-Standard with identical settings at each startup

Problem: trouble getting decent intensities despite alignment check
  Solution: check age of notch filter and replace with edge filter ;-)

Problem: Peak precision to within ±1cm-1
  Solution: calibrate system to 520.6 ±0.1 cm-1 at each startup using external Si-wafer

Problem: Fluorescence on paint samples with 514 or 633nm lasers
  Solution: begin with 785nm excitation

Problem: reaching saturation and still only weak signals (Quinacridones)
  Solution: Set camera gain low to reduce count rate, while maintaining or increasing the required excitation

Problem: documentation of OH groups
  Solution: check detector efficiency range, e.g. 785nm cuts of at 3200cm-1, use 514 or 633nm laser instead

5 Problems encountered and possible solutions

Problem: heat input with 785nm excitation / thermal stability of substance
Solution: always work with pinhole in (Renishaw), begin at 1% or ~0.12mW P_{sample} and check spot after analysis. ATTENTION! Some compounds may alter upon heat input and produce a different spectrum (e.g. Phthalocyanines)

Problem: smell of sulfur after measurement
Solution: reduce laserpower and change spot, you just burnt HgS

Problem: peak shifting observed with Phthalocyanines (Pc)
Solution: check spot, reduce laserpower until main band doesn't shift any more

Problem: similar bands but no perfect match with reference (e.g. Pc)
Solution: compare spectra of same excitation wavelength

Problem: difficulty producing decent spectra with 'extendable arm'
Solution: 50x Objective requires perfect positioning and focusing. Use a precision stage and external illumination for proper orientation and focusing.

…

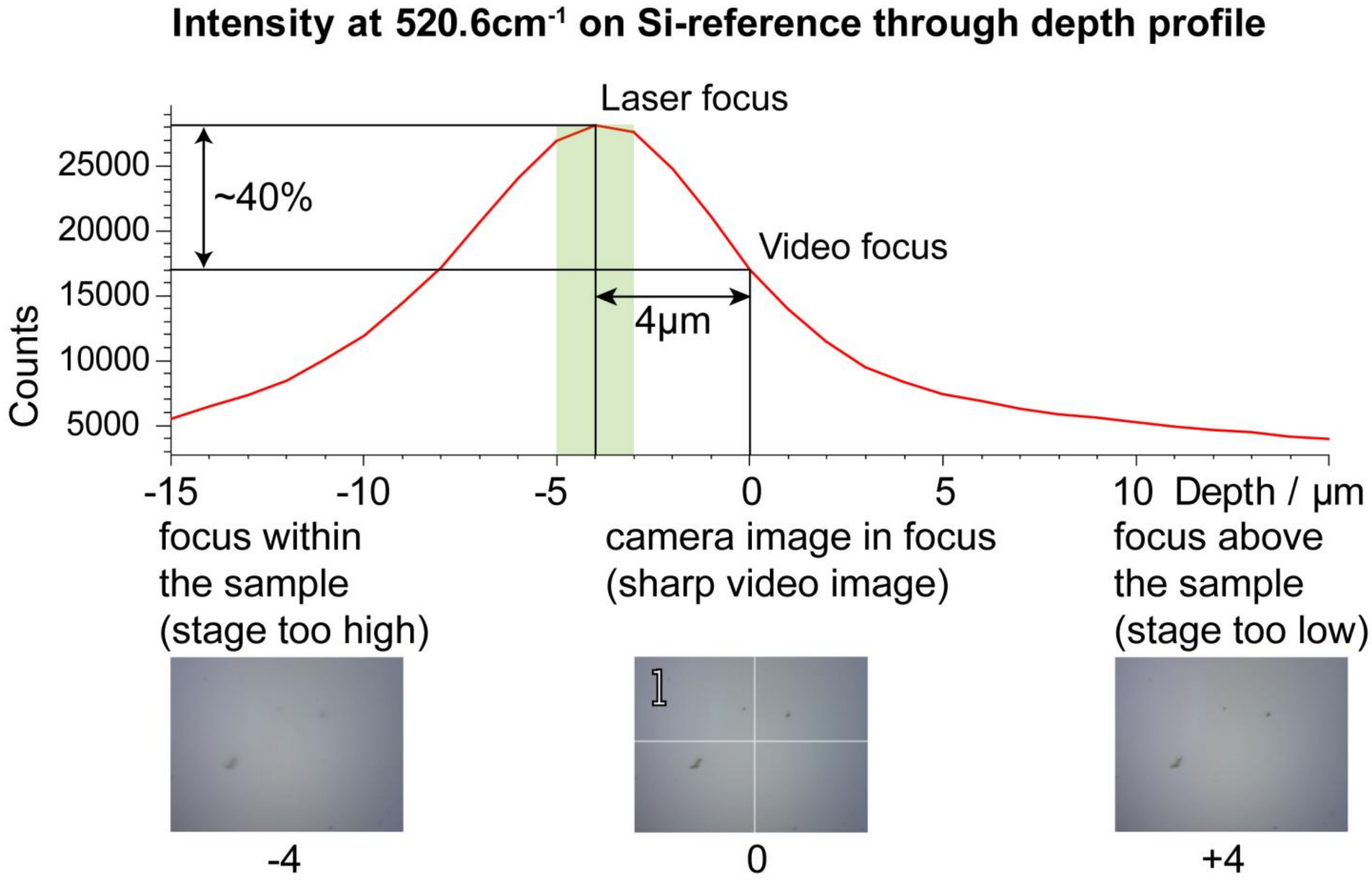
5 *Calibration of the system*

- After warm-up – use 'quick calibration' function
- control measurement on an external Si-wafer
- 100% laserpower / 1s / 10accumulations / pinhole IN
- Adjust calibration until Si-peak is within 520.6 ± 0.1cm-1
- Compare counts with previous calibrations
- If counts too low, go through the automatic alignment procedures

5 *Analytical strategy with paint analysis*

- Start with **785nm** laser, **always** with **pinhole IN**
- Start with **1%** laserpower (P_s 1.21mW), 10s, 1acc. over full range
- Visually **check spot** after each analysis and laserpower increase
- Adjust laserpower, acquisition time, number of accumulations
- If no bands obvious, but saturated
  1. Reduce laser power, if no succes, then
  2. Increase laser power, set detector setting "camera low" (e.g. with quinacridones, which seem to require a minimum level of excitation energy, but this in turn requires to counteract saturation
  3. If only systematic wavy background, go to next sample

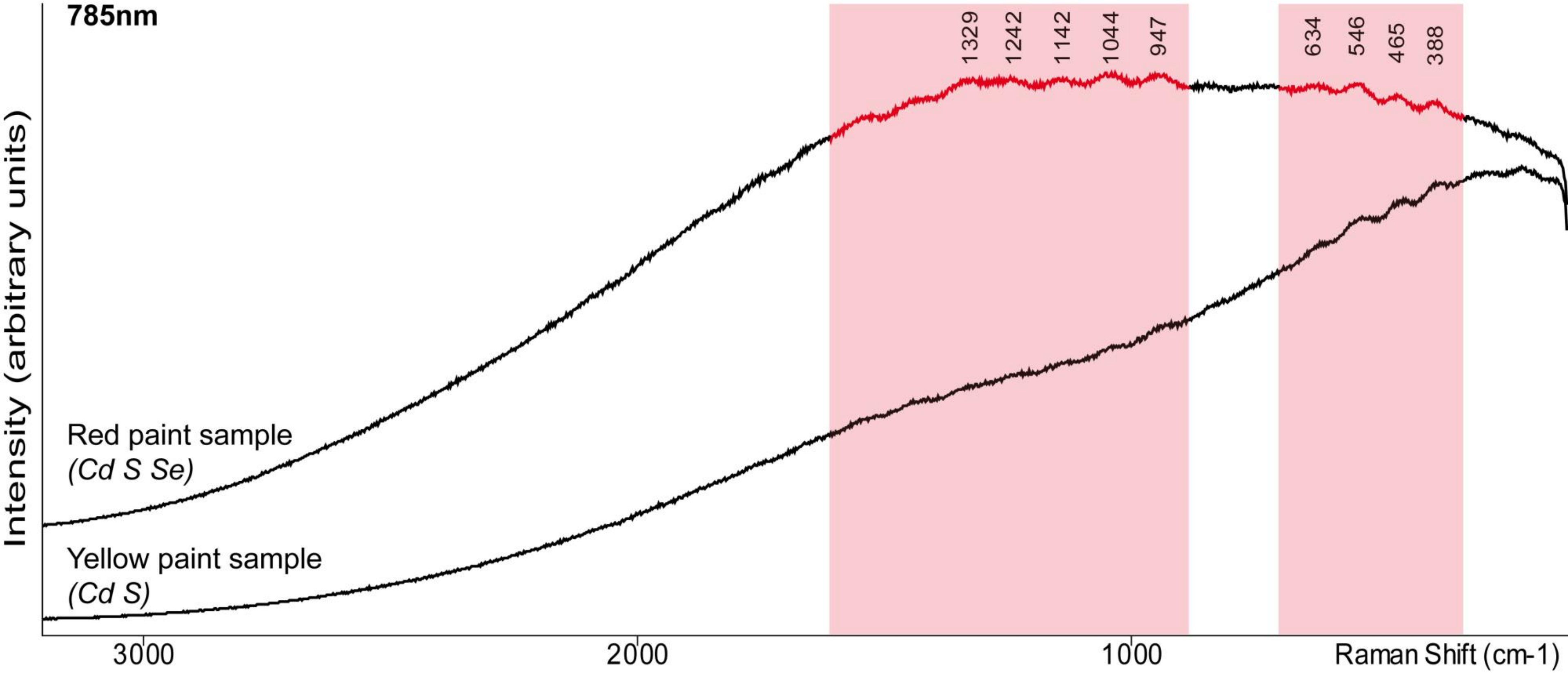
5 *Focus/depth versus signal intensity*



Intensity at $520.6 cm^{-1}$ on Si-reference through depth profile

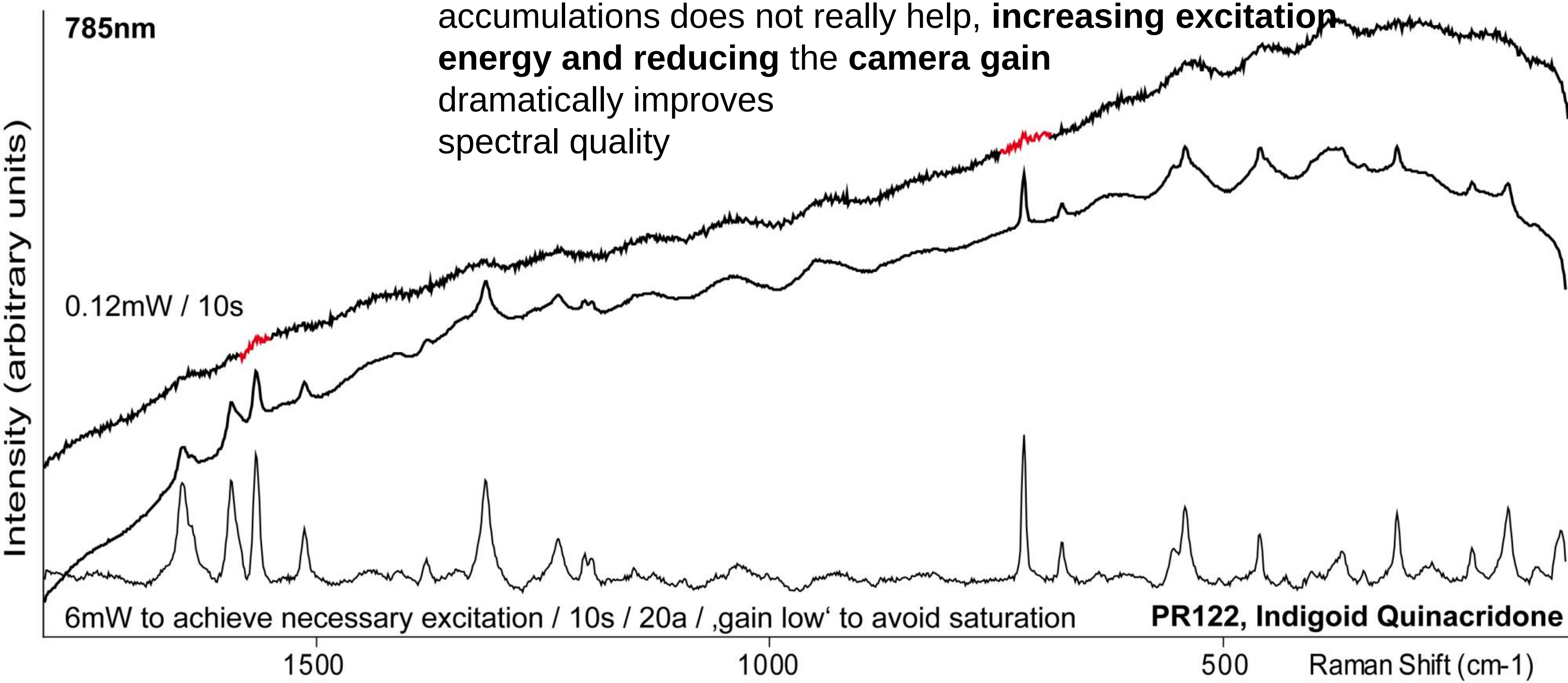
5 *Problems – wavy background, no response*

- Background with systematic broad waves: try a few spots, perhaps improve signal to noise ratio and if there is no sign of sharp bands, don't waste your time on this laser/sample combination

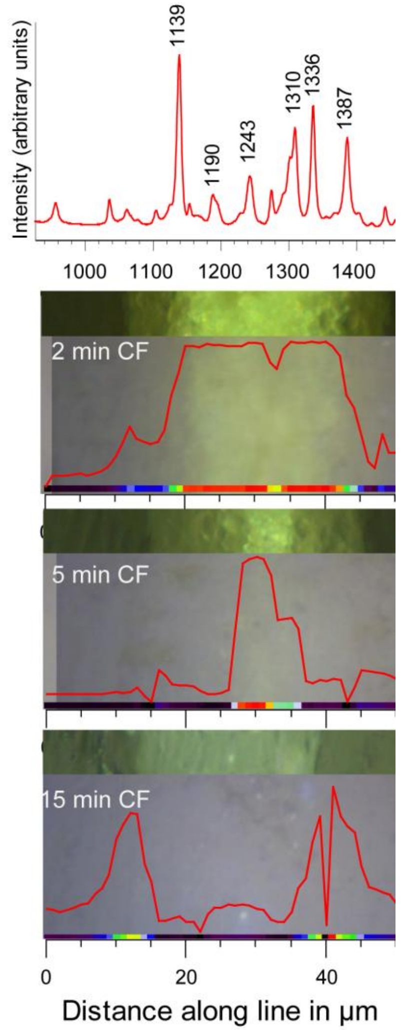


5 *Problems – poor response on Quinacridones Minimum excitation energy vs detector saturation*

- **Quinacridones** have a high fluorescence background, causing detector saturation already at low power very quickly.
- While decreasing the laser power and increasing the no. of accumulations does not really help, **increasing excitation energy and reducing** the **camera gain** dramatically improves spectral quality



PY3 Hansagelb
Schmicke Norma Prof. No. 236
Paintfilm after treatment with chloroform (CF) embedded in Technovit 2000 LC



5 *Efficiency of linescan or mapping experiments*

Linescan or mapping experiments are time consuming. Customizing analytical settings to the sample prior to running a series of line profiles or mappings is essential to make it worthwhile…

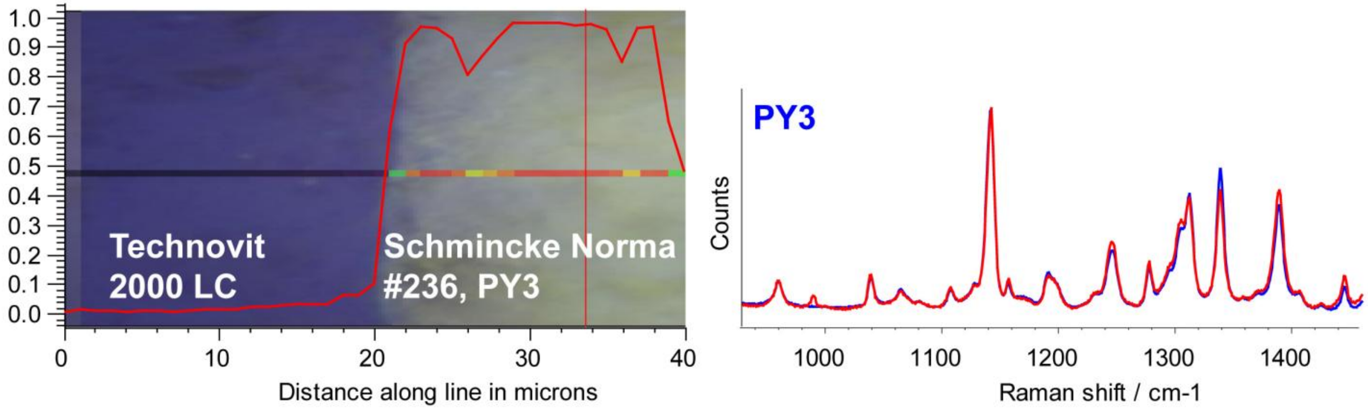
- Optimize laser power, acquisition time, number of scans
- Minimize time per spot
- Use static mode (1s interval), but check best spectral window to cover all phases of interest with distinctive bands

  - Experiment settings:
  - Laser: 785nm / Grating: 1200 l/mm
  - Laserpower: 100%, ~12.1 Mw on sample
  - Mode: static, centred on 1200 cm-1 (covering 950 to 1450 cm-1)
  - Scan time: 4 s / Accumulations: 6
  - Total acquisition time per spot = 24s / Time profile 40 µm ~ 20 min
  - Objective: 100x standard / Step size: 1 µm

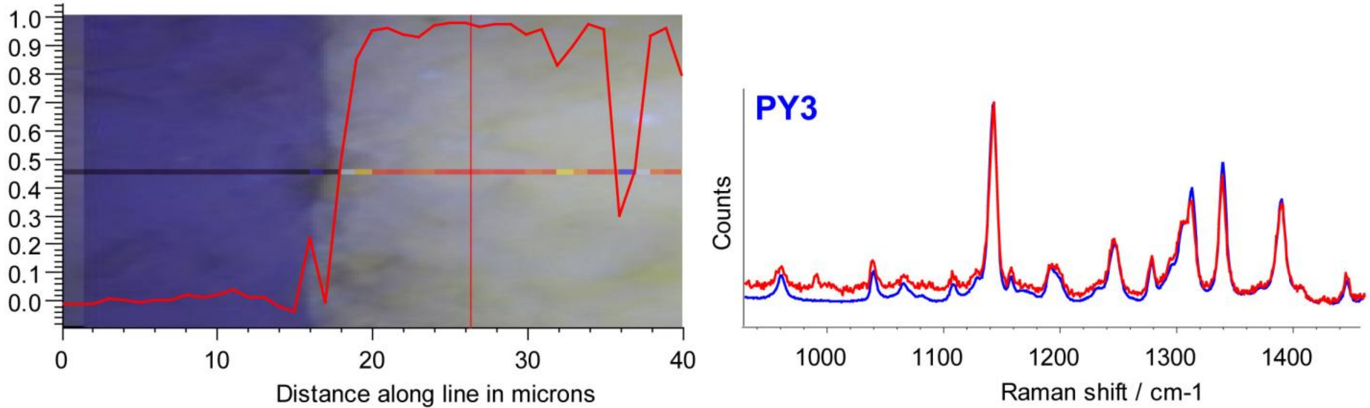
5 *Efficiency of linescan or mapping experiments*

Does a smaller slit size and confocality 'high' improve spatial resolution?

Slit size 65 µm

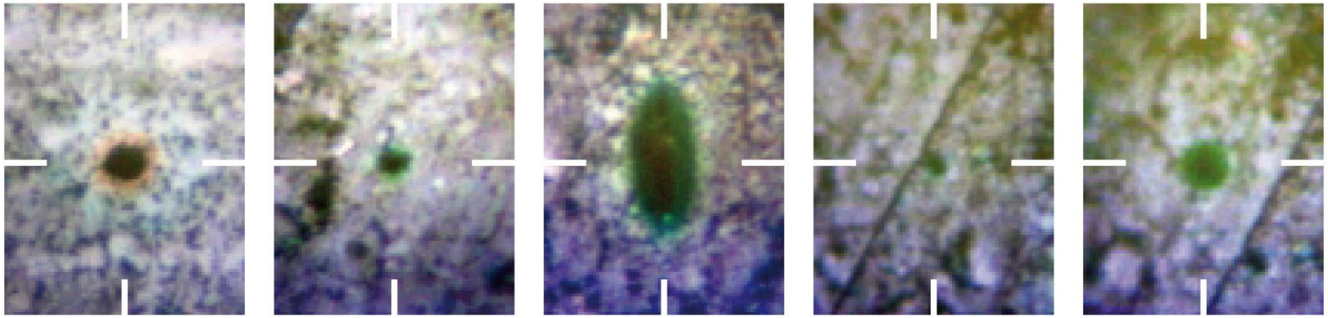


Slit size 20 µm



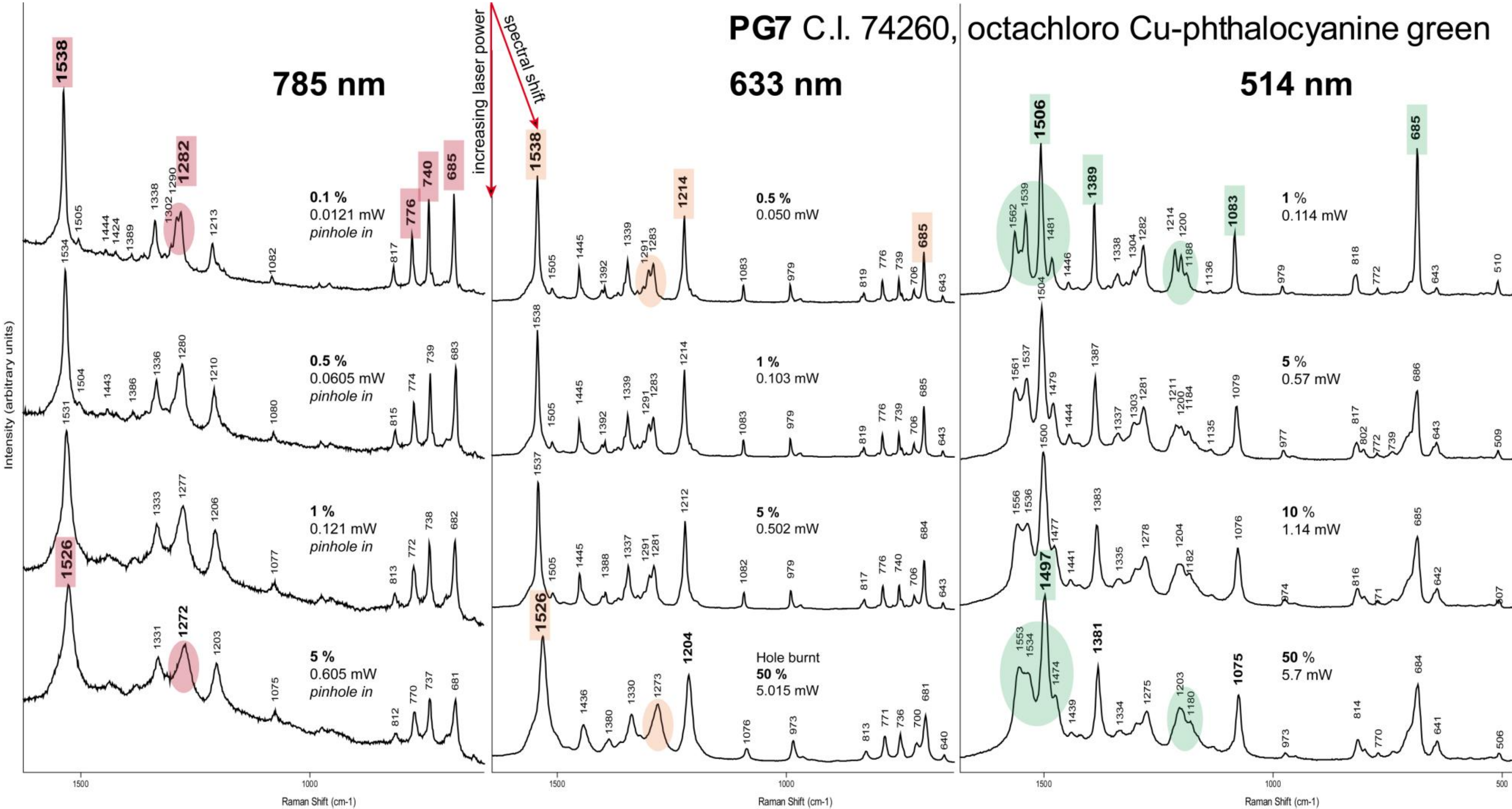
5 *Visual spot alteration and peak shifting with Pc*

Excessive laserpower: visible alteration on PG7



514 nm	633 nm	785 nm	785 nm	785 nm
		pinhole out	*pinhole in*	*pinhole in*
50%	**50 %**	**0.5%**	**5%**	**10%**
5.7 mW	5.015 mW	0.0605 mW	0.605 mW	1.21 mW

5 *Peak shifting due to excessive energy on Pc*



6 Spectral interpretation

- **Inorganic pigments**: only **few bands**
  - Use published tables or existing databases

- **Synthetic organic pigments**: **large number of bands**.
  - Tables of limited use, require systematic approach e.g. flowchart
  - Limited availability of reference databases
  - **Very efficient using** e.g. Spectral ID **database peak matching**
  - **Spectra matching ideally** performed on spectra of **same excitation wavelength**

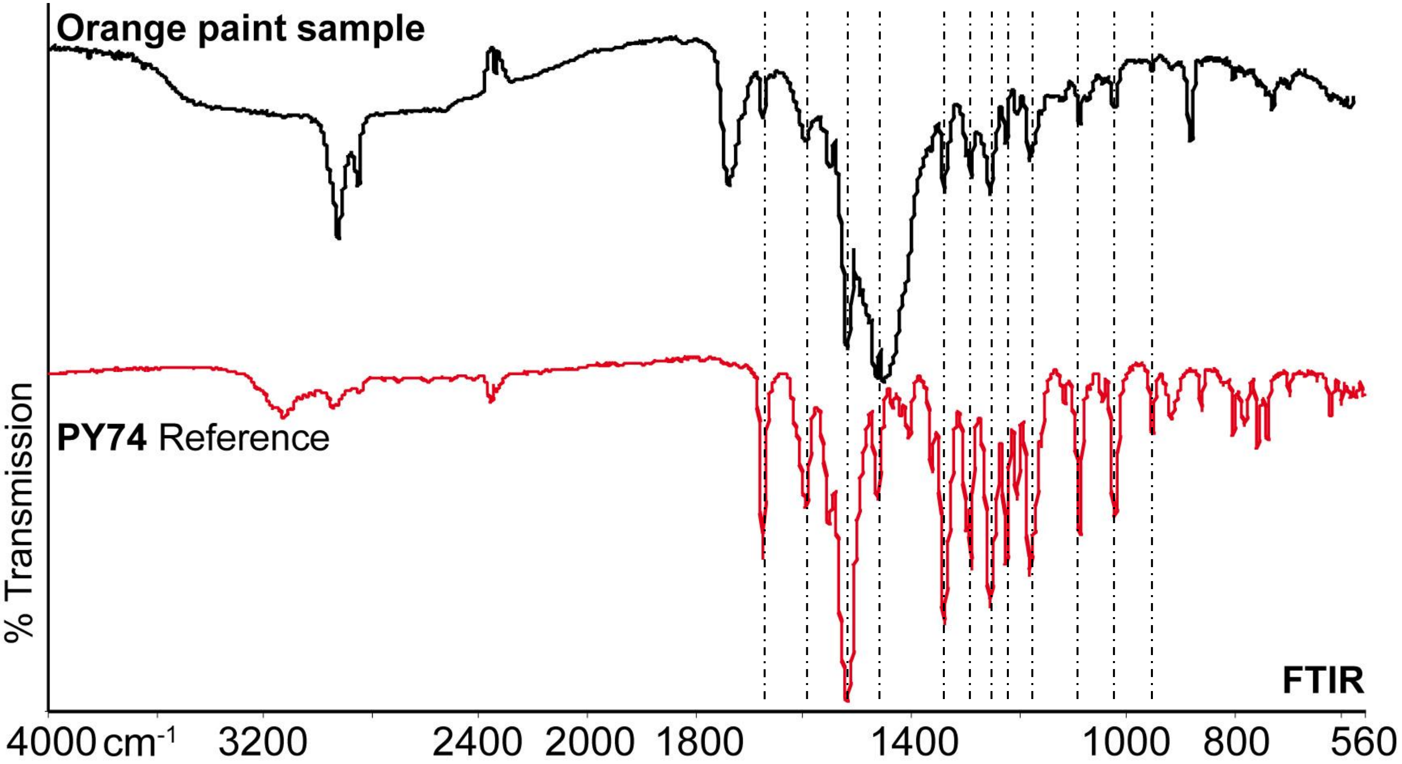
  - **Mixed synthetic organic pigments** require user interaction
  - Searching references for minor components facilitated with **peak / relative intensity database** searching non-overlapping strong signals and efficiently **reduce the number** of potential **candidates**

  - **Low intensity** of **binder** eases spectrum search on **paint samples**

6 **FTIR:** *Sensitivity to interfering compounds*

Painting declared as "Les bucherons" signed with "N. Goncharova 1911" *(1888 to 1962)*

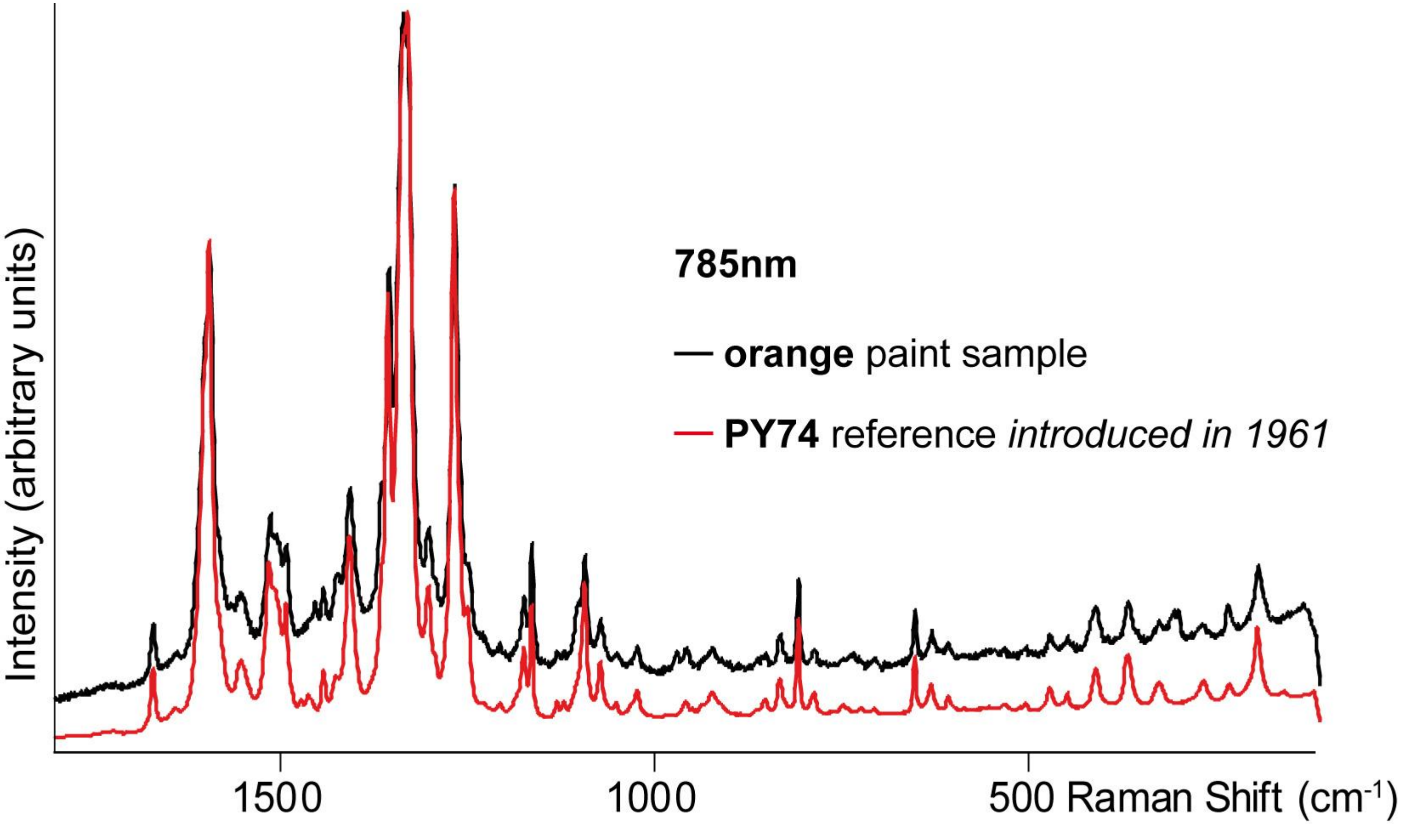
- synthetic organic pigment often hidden by binder and filler
- simultaneous gain of information on multiple paint components
- sample preparation required



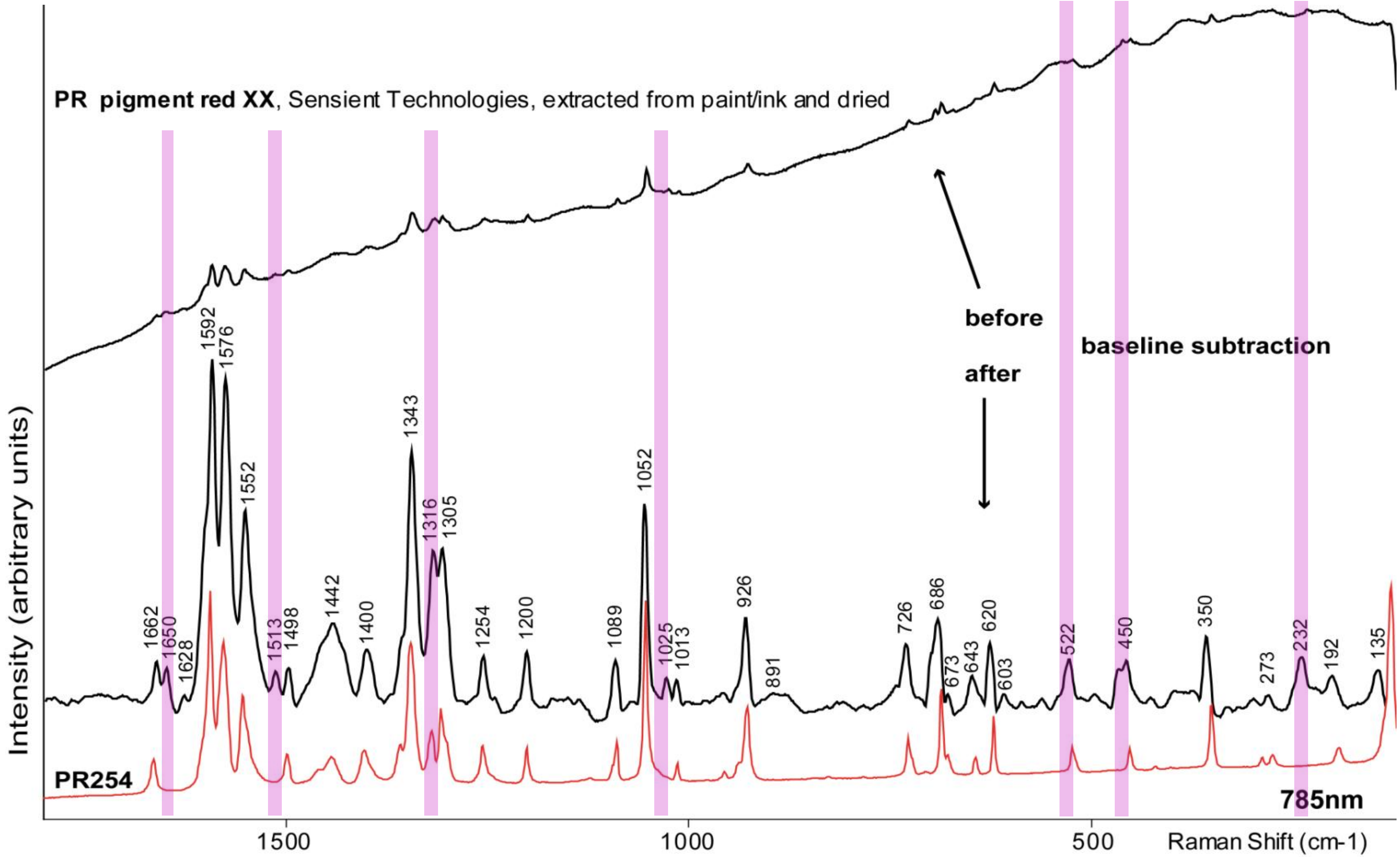
6 **Raman:** *Sensitivity to interfering compounds*

- high signal intensity on synthetic organic pigment
- easy identification with automated spectrum search
- yet no information on binder system
- no sample preparation

Painting declared as "Les bucherons"
signed with "N. Goncharova 1911"
(1888 to 1962)



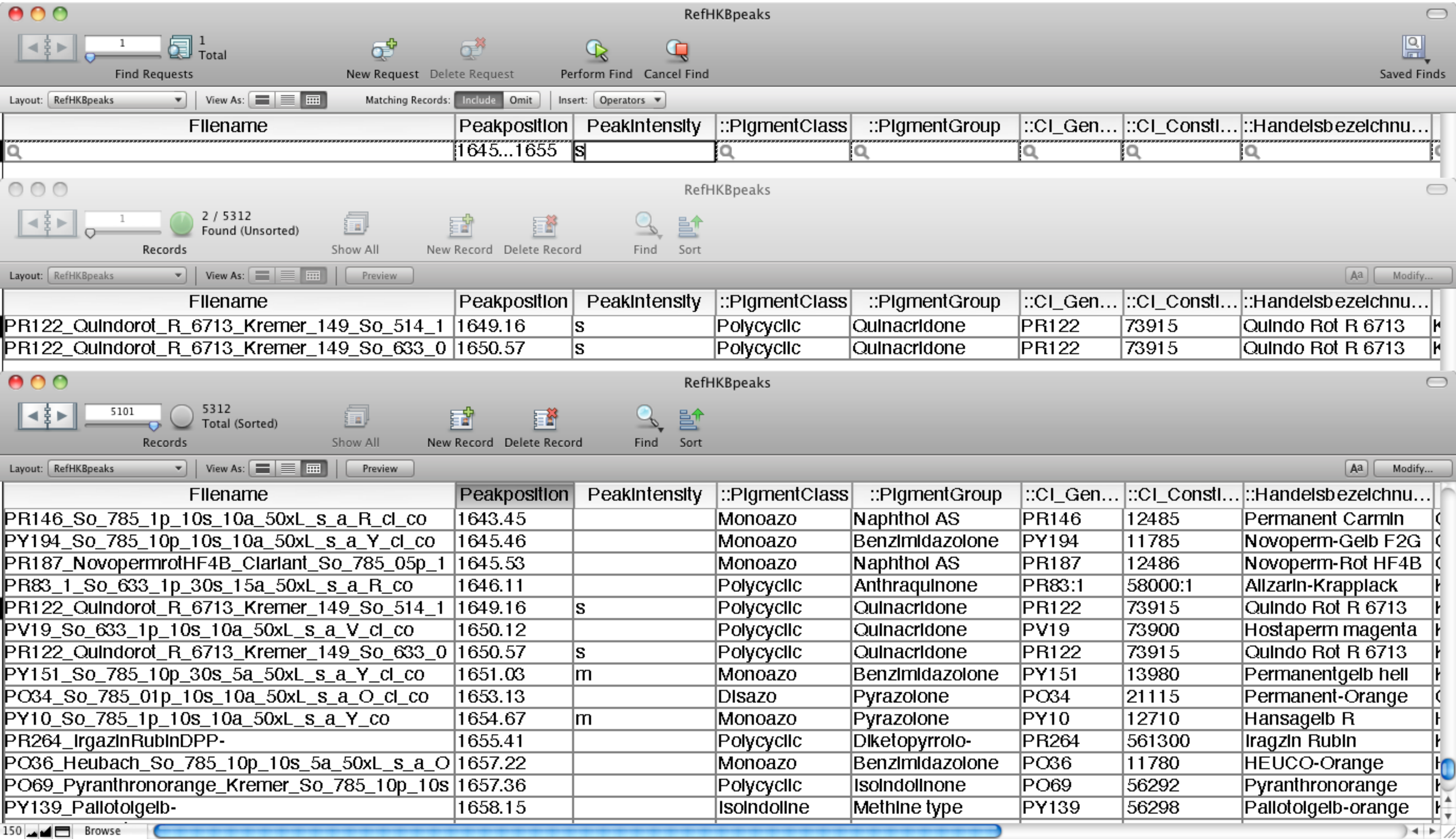
6 Spectral interpretation *in pigment mixtures*



PR pigment red XX, Sensient Technologies, extracted from paint/ink and dried

before / **after** **baseline subtraction**

6 Spectral interpretation *in pigment mixtures*



Find request: 1 / 1 Total; Layout: RefHKBpeaks

Filename	Peakposition	PeakIntensity	::PigmentClass	::PigmentGroup	::CI_Gen…	::CI_Consti…	::Handelsbezeichnu…
	1645...1655	s					

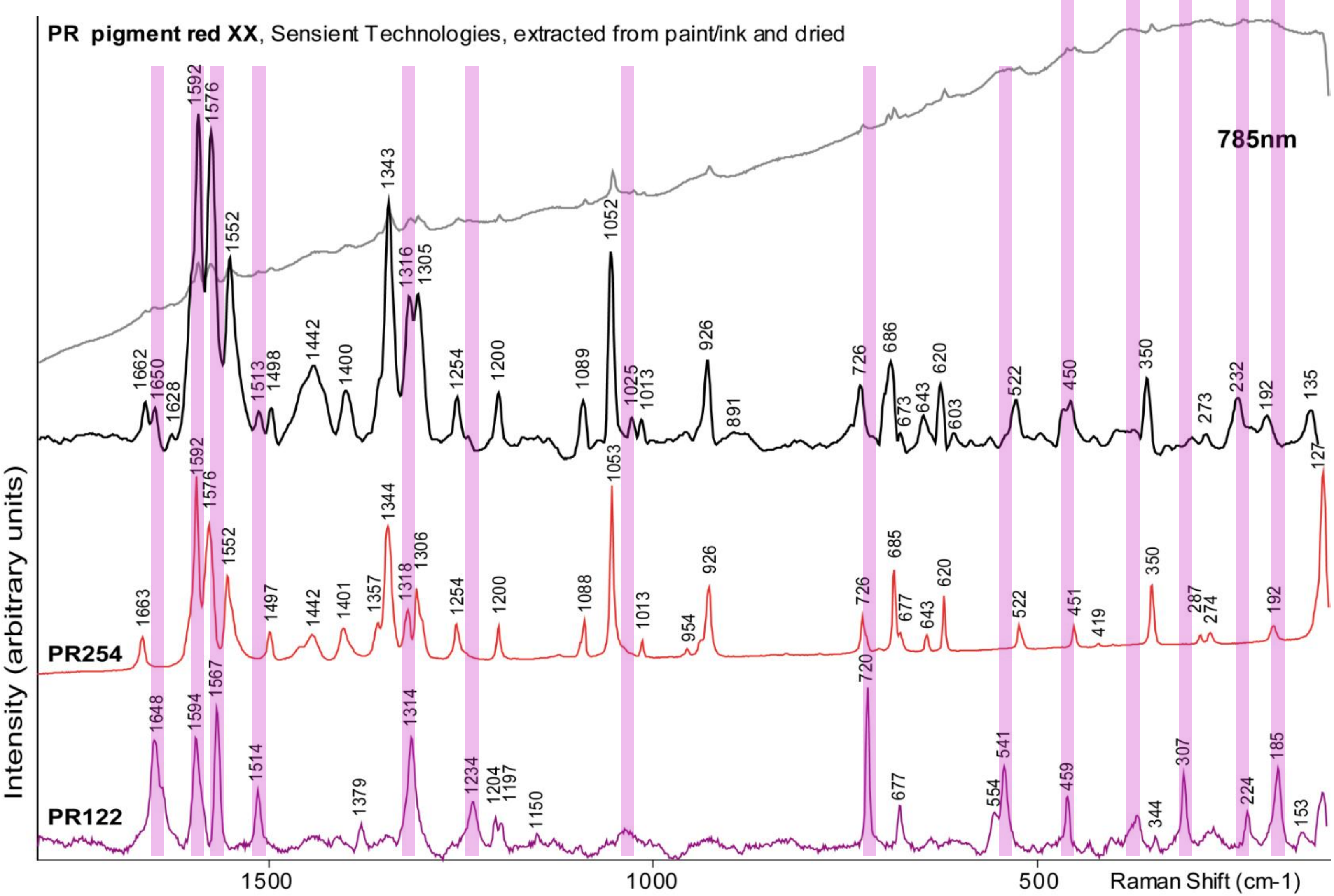
Records: 1 — 2 / 5312 Found (Unsorted); Layout: RefHKBpeaks

Filename	Peakposition	PeakIntensity	::PigmentClass	::PigmentGroup	::CI_Gen…	::CI_Consti…	::Handelsbezeichnu…
PR122_Quindorot_R_6713_Kremer_149_So_514_1	1649.16	s	Polycyclic	Quinacridone	PR122	73915	Quindo Rot R 6713
PR122_Quindorot_R_6713_Kremer_149_So_633_0	1650.57	s	Polycyclic	Quinacridone	PR122	73915	Quindo Rot R 6713

Records: 5101 — 5312 Total (Sorted); Layout: RefHKBpeaks

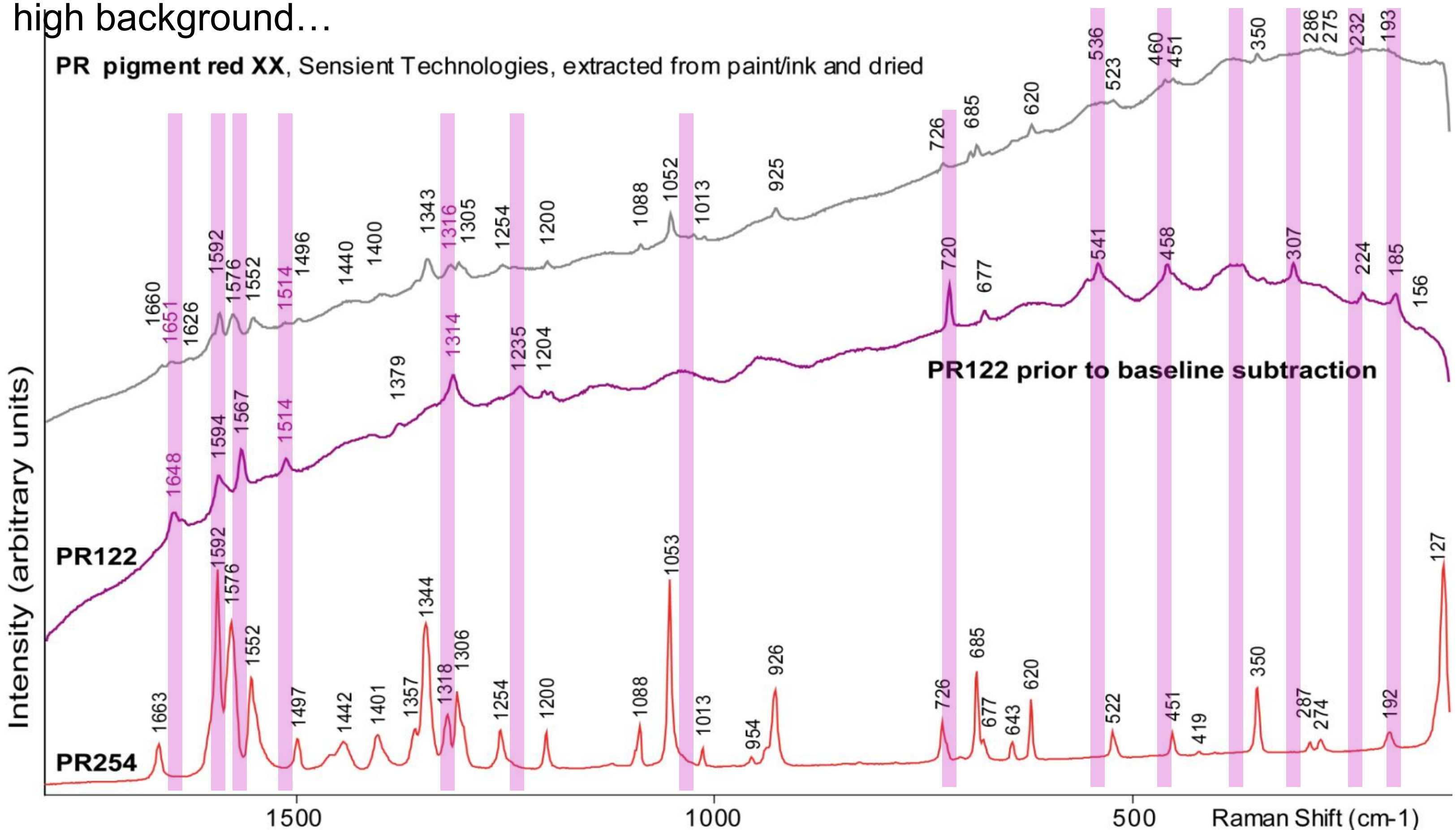
Filename	Peakposition	PeakIntensity	::PigmentClass	::PigmentGroup	::CI_Gen…	::CI_Consti…	::Handelsbezeichnu…
PR146_So_785_1p_10s_10a_50xL_s_a_R_cl_co	1643.45		Monoazo	Naphthol AS	PR146	12485	Permanent Carmin
PY194_So_785_10p_10s_10a_50xL_s_a_Y_cl_co	1645.46		Monoazo	Benzimidazolone	PY194	11785	Novoperm-Gelb F2G
PR187_NovopermrotHF4B_Clariant_So_785_05p_1	1645.53		Monoazo	Naphthol AS	PR187	12486	Novoperm-Rot HF4B
PR83_1_So_633_1p_30s_15a_50xL_s_a_R_co	1646.11		Polycyclic	Anthraquinone	PR83:1	58000:1	Alizarin-Krapplack
PR122_Quindorot_R_6713_Kremer_149_So_514_1	1649.16	s	Polycyclic	Quinacridone	PR122	73915	Quindo Rot R 6713
PV19_So_633_1p_10s_10a_50xL_s_a_V_cl_co	1650.12		Polycyclic	Quinacridone	PV19	73900	Hostaperm magenta
PR122_Quindorot_R_6713_Kremer_149_So_633_0	1650.57	s	Polycyclic	Quinacridone	PR122	73915	Quindo Rot R 6713
PY151_So_785_10p_30s_5a_50xL_s_a_Y_cl_co	1651.03	m	Monoazo	Benzimidazolone	PY151	13980	Permanentgelb hell
PO34_So_785_01p_10s_10a_50xL_s_a_O_cl_co	1653.13		Disazo	Pyrazolone	PO34	21115	Permanent-Orange
PY10_So_785_1p_10s_10a_50xL_s_a_Y_co	1654.67	m	Monoazo	Pyrazolone	PY10	12710	Hansagelb R
PR264_IrgazinRubinDPP-	1655.41		Polycyclic	Diketopyrrolo-	PR264	561300	Iragzin Rubin
PO36_Heubach_So_785_10p_10s_5a_50xL_s_a_O	1657.22		Monoazo	Benzimidazolone	PO36	11780	HEUCO-Orange
PO69_Pyranthronorange_Kremer_So_785_10p_10s	1657.36		Polycyclic	Isoindolinone	PO69	56292	Pyranthronorange
PY139_Pallotolgelb-	1658.15		Isoindoline	Methine type	PY139	56298	Pallotolgelb-orange

6 Spectral interpretation *in pigment mixtures*

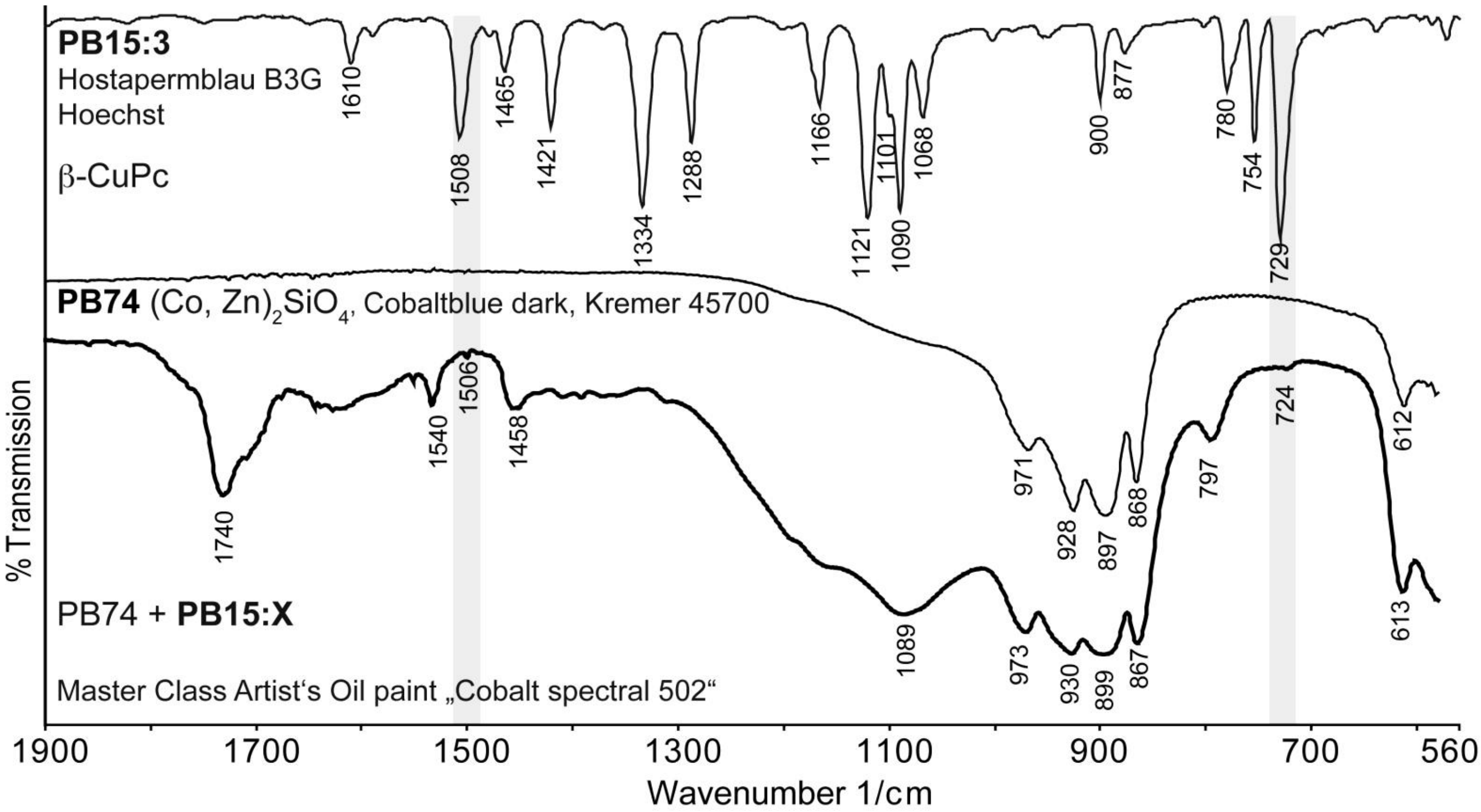


6 **Spectral interpretation** *in pigment mixtures*

We may deduce: The small amount of Quinacridone PR122 in this pigment mixture PR254 + PR122 seems to explain the high background or the background pattern of the unknown mixture supports the presence of a minor component producing a high background…

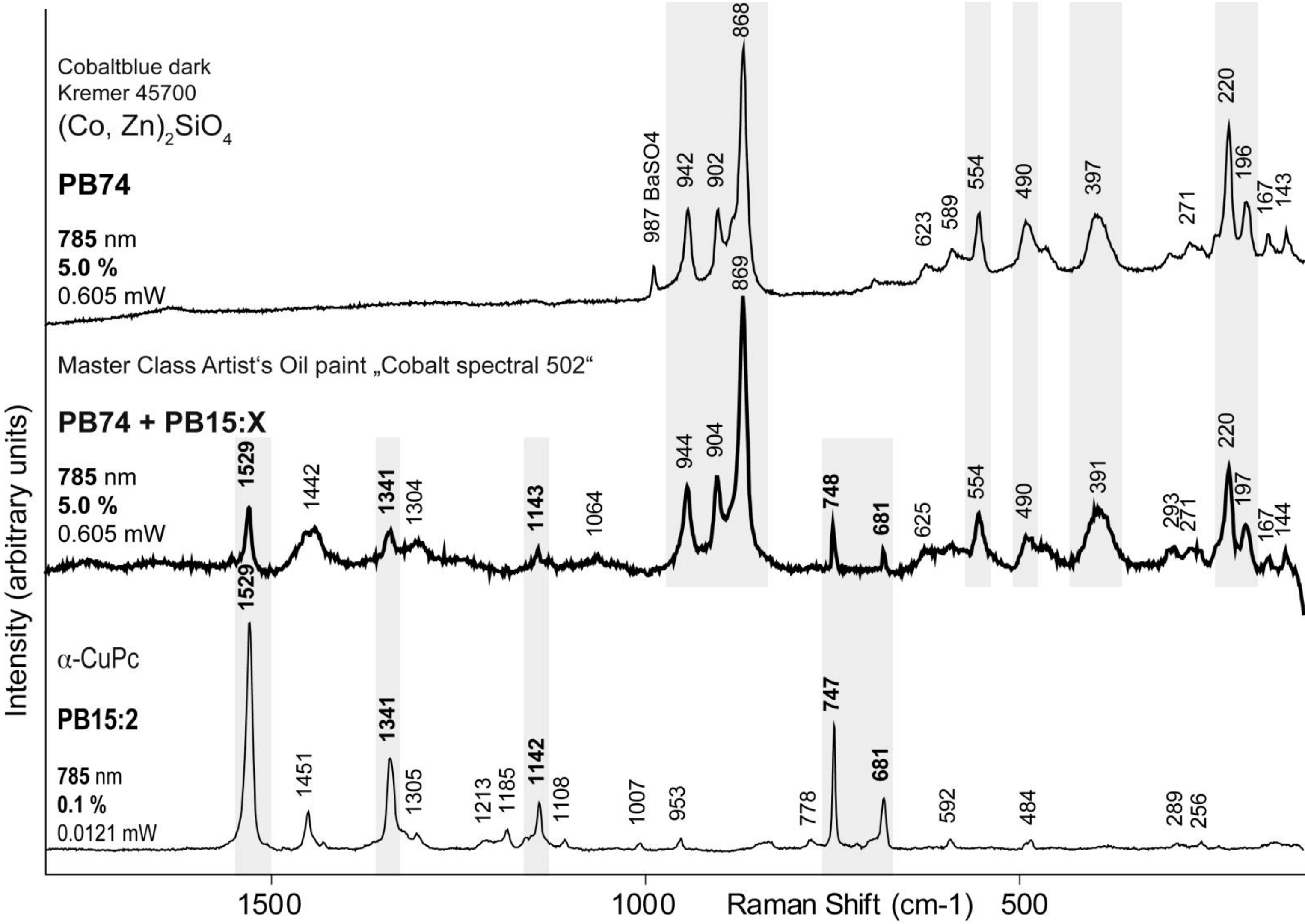


6 Spectral interpretation, *pure powder vs paint*



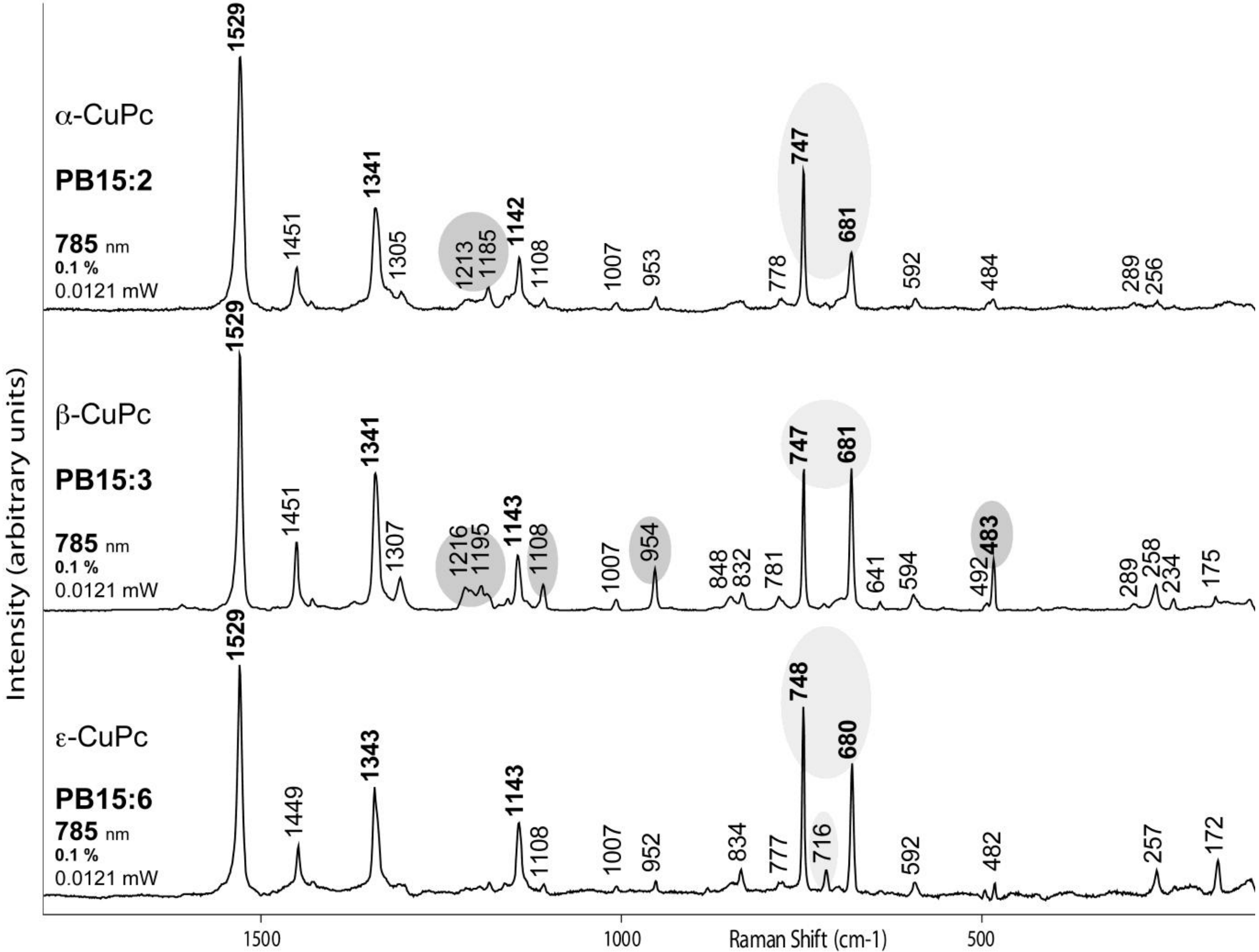
FTIR

6 Spectral interpretation, *pure powder vs paint*

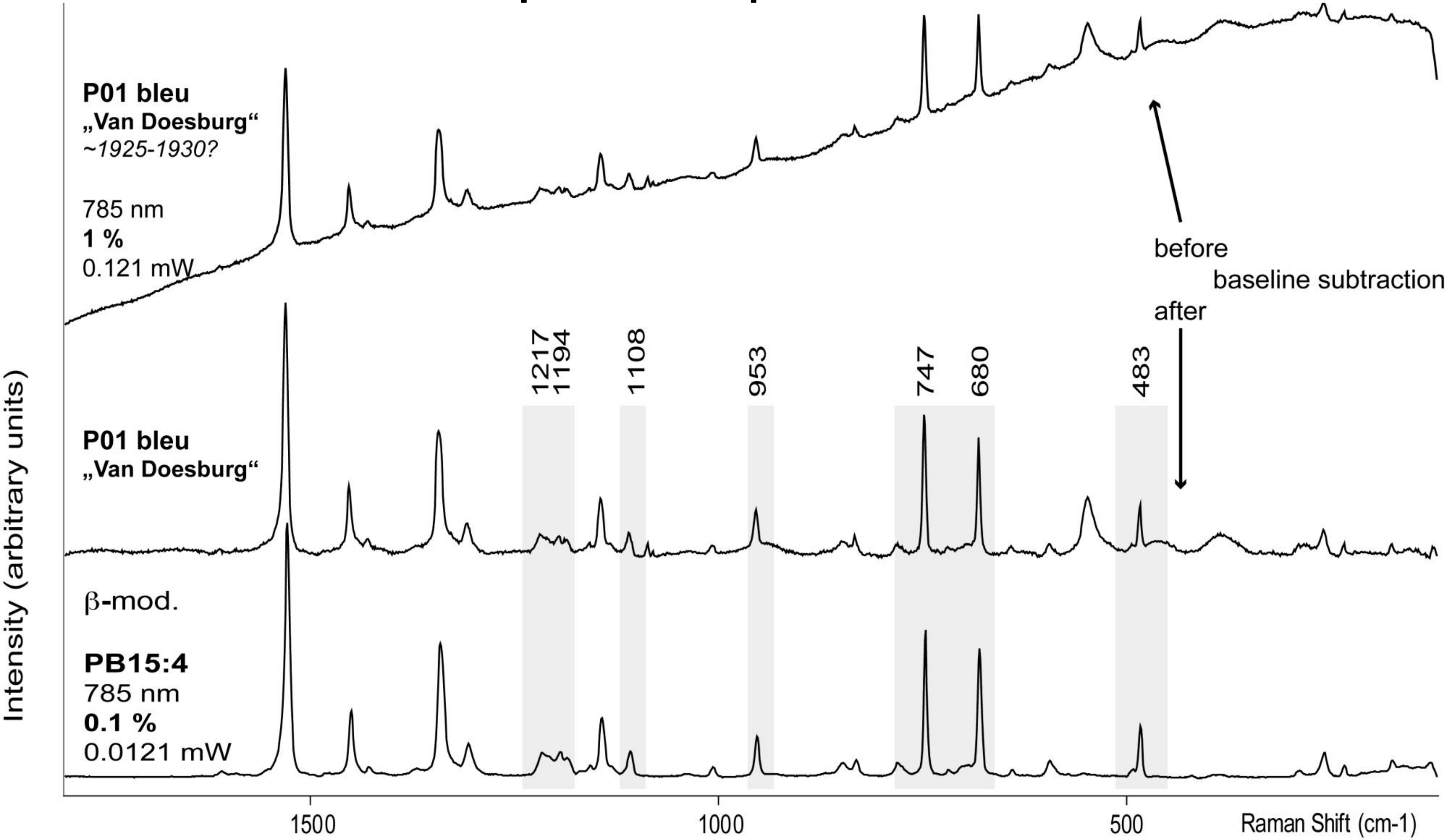


RAMAN

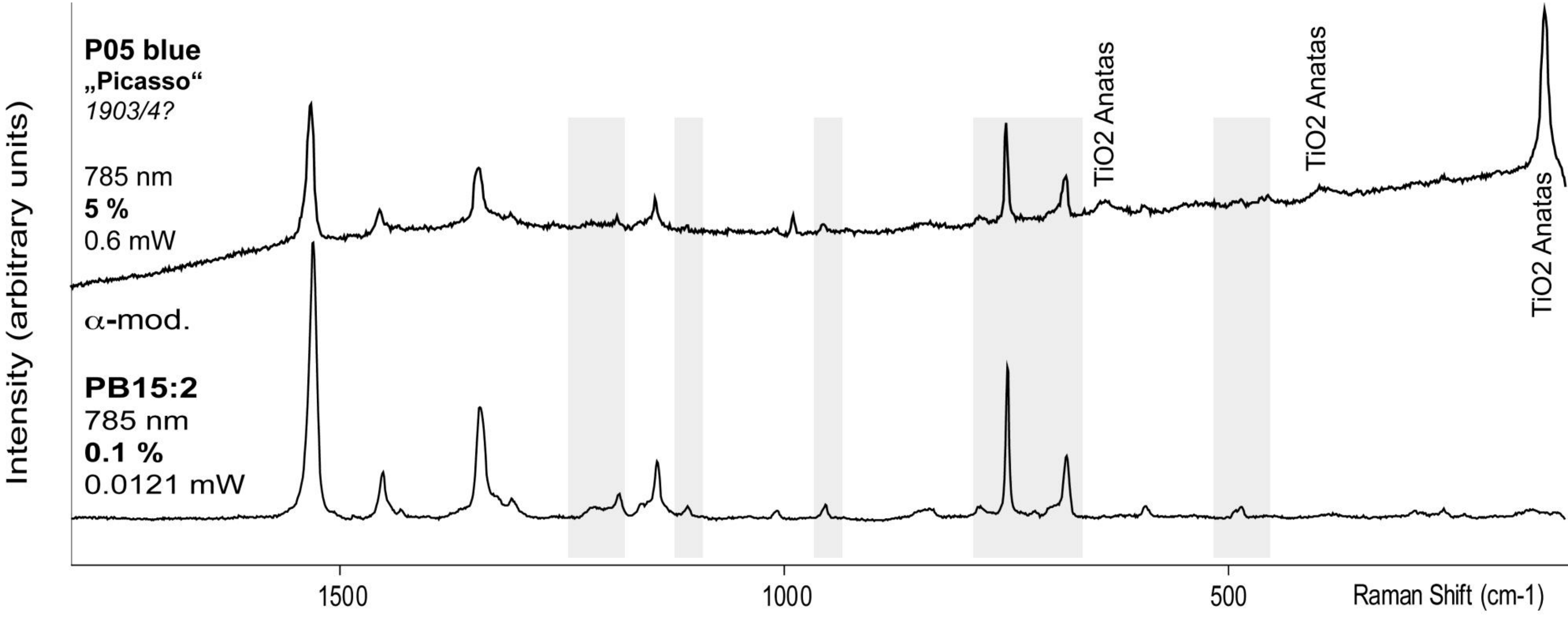
6 **Spectral interpretation** *of PB15 modifications*



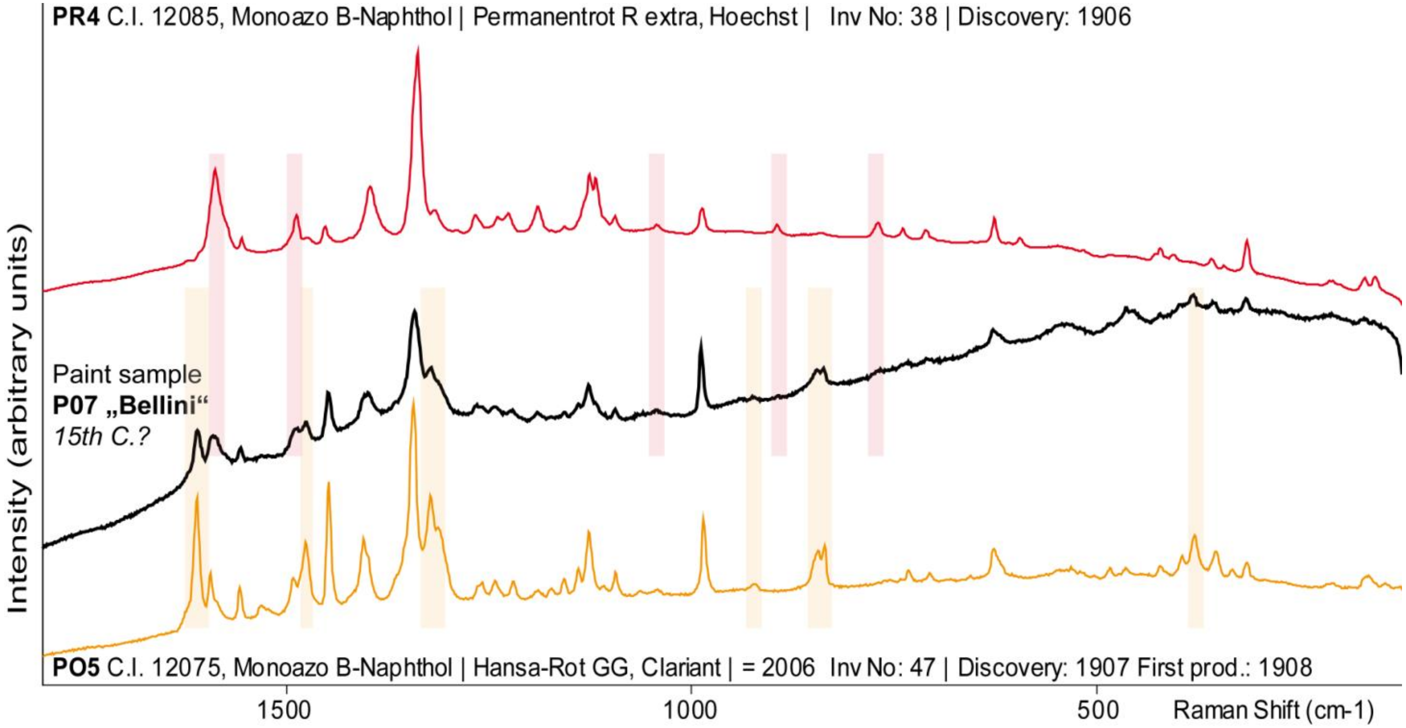
6 **Spectral interpretation** *of PB15 modifications*



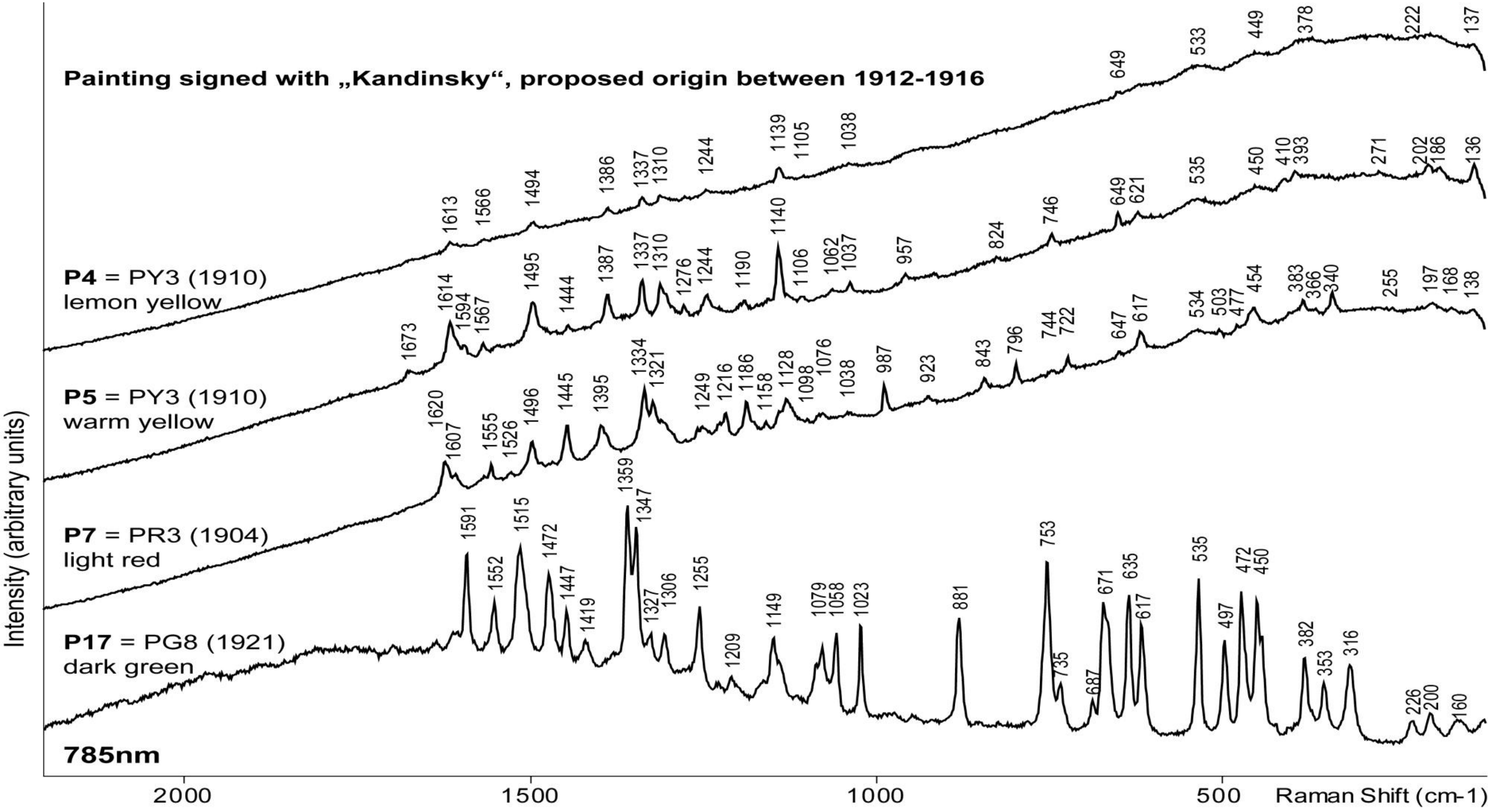
6 Spectral interpretation *of PB15 modifications*



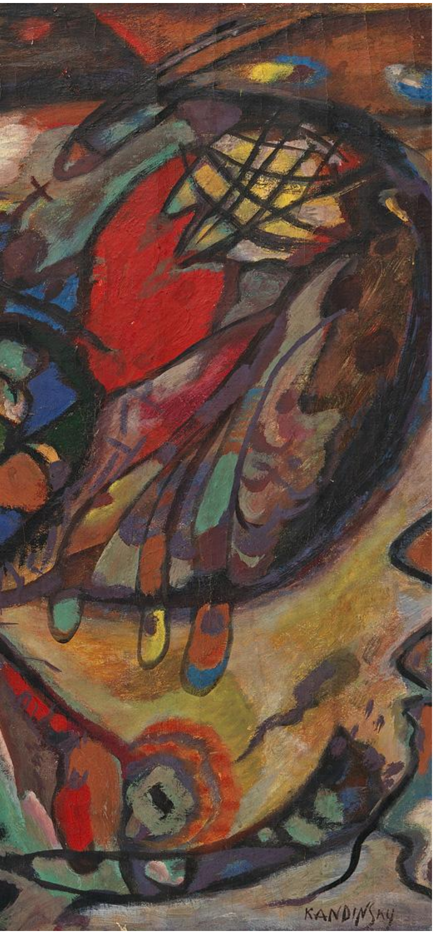
7 Case studies

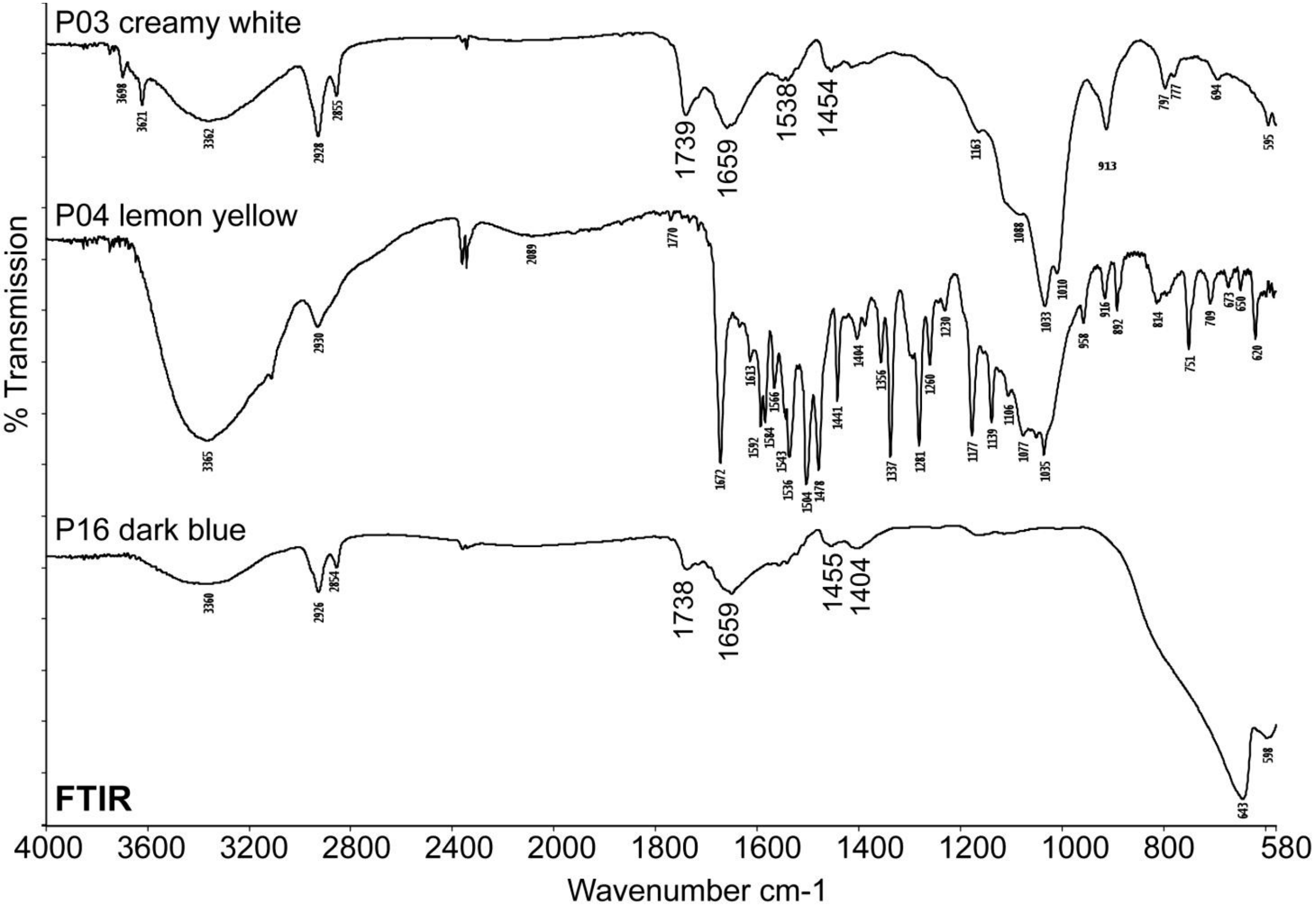


7 Case studies



7 Case studies





8 Advantages and limitations

Advantages

- Very **powerful** on **synthetic organic pigments** with a good reference database in the back
- **electronic spectra matching** quite powerful (helpful to non-chemists)
- No or minimal sample preparation, delivers in most cases a quick answer on synthetic organic pigments using 785nm excitation
- **Accessibility** through transparent materials below surface
- Minimal sample quantity or even in-situ

Disadvantages

- No or poor information on binder system
- No or poor information on accumulated degradation products as a factor of ageing
- Mapping on paint crosssections limited
- Ideally combined with other techniques such as SEM and FTIR
- Response not guaranteed… experience is of great advantage ;-)

9 Summary

Whilst there are many advantages of Raman spectroscopy to the identification of synthetic organic pigments in paint samples, experience with the instrument and on the response of different material combinations comes in very handy.

With the many parameters that require adjustment for successful and good quality spectra, the technique is perhaps less suited to occasional use only. This is where FTIR is perhaps more student friendly in the handling. When it comes to interpretation with the help of electronic spectra matching, Raman in turn can be considered more user friendly – as long as you have complete database.

The widespread use of synthetic organic pigments also in artist's paints, the accessible chronological information on a wide range of these, and the ease of detection with Raman spectroscopy make it a great tool not only in forensic applications…

Acknowledgements

- Bern University of the Arts for sponsoring and infrastructure
- SIK-ISEA Zurich for access to artwork and samples
- The friendly invitation by Beth Price
- The patience and support of my wife and kids...

Infrared & Raman Users Group

Raman Spectroscopy Workshop

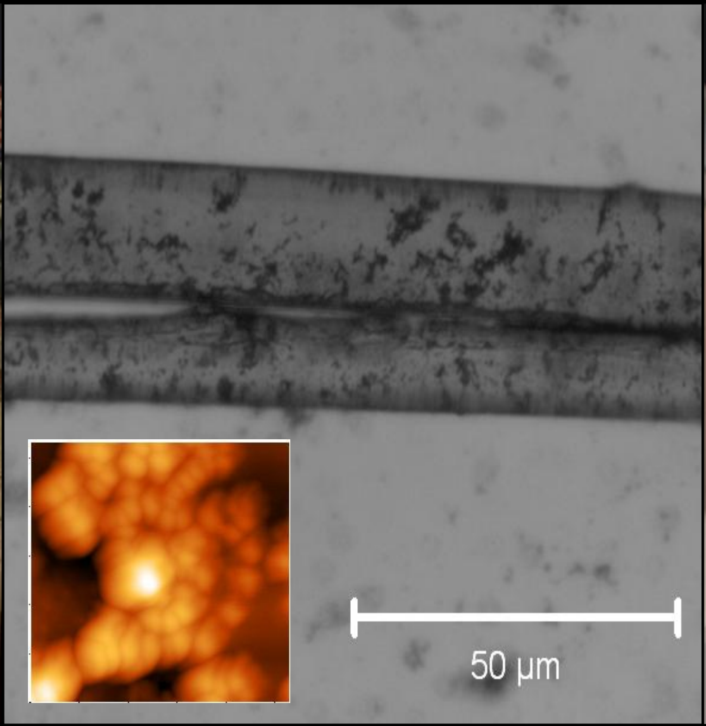
Surface-enhanced Raman scattering (SERS) of natural & synthetic colorants

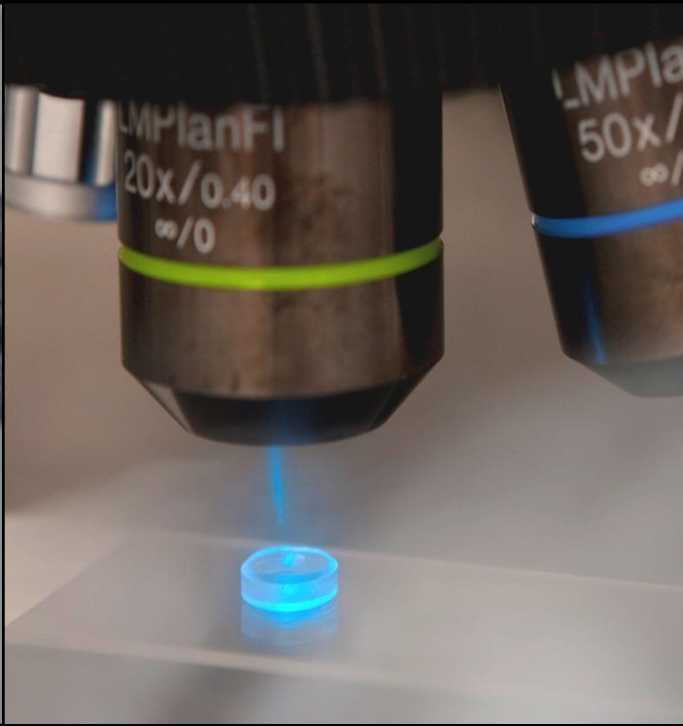
Marco Leona

Metropolitan Museum of Art, New York, US

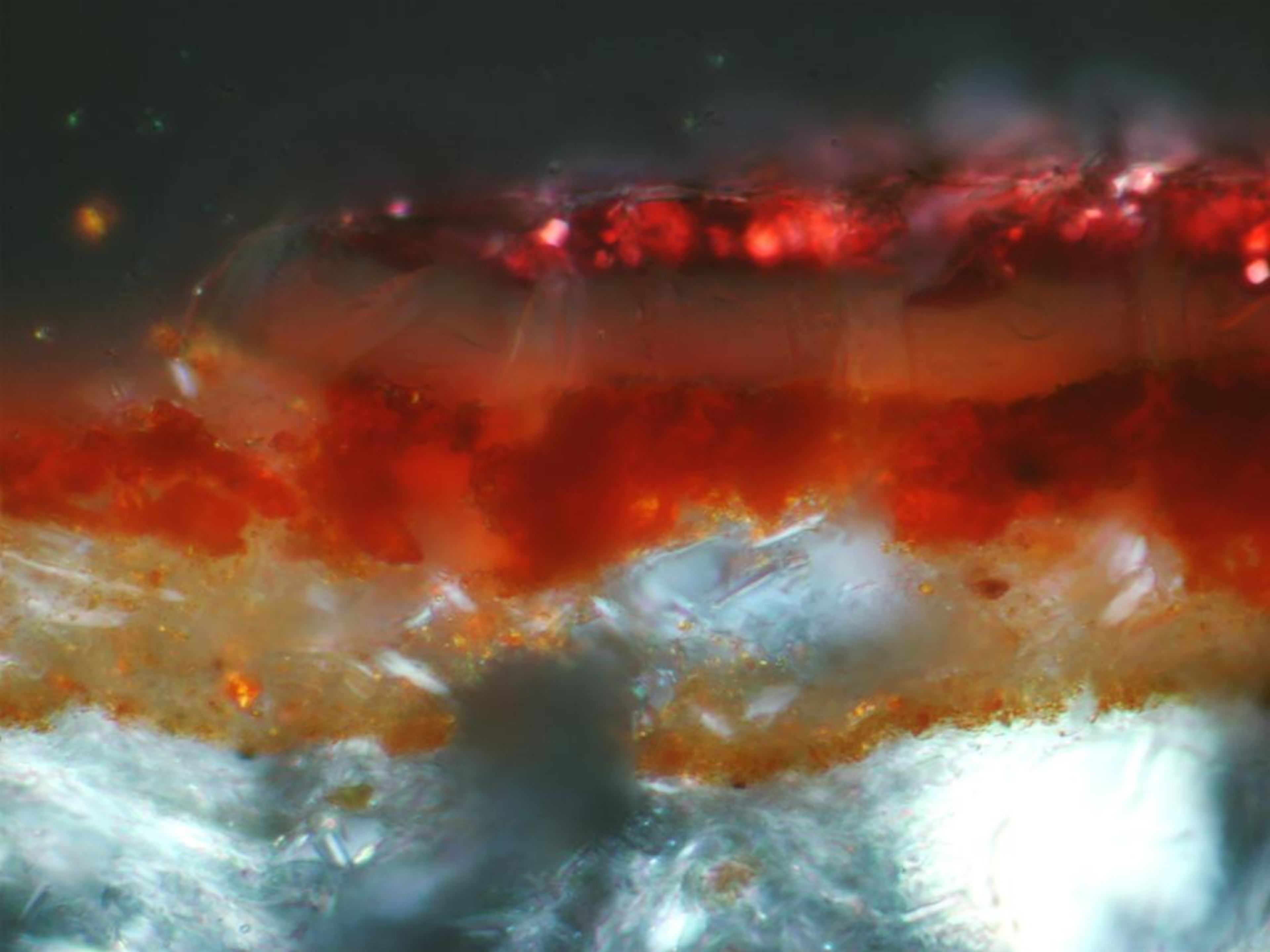
FRIDAY, SEPTEMBER 28: LECTURE 3

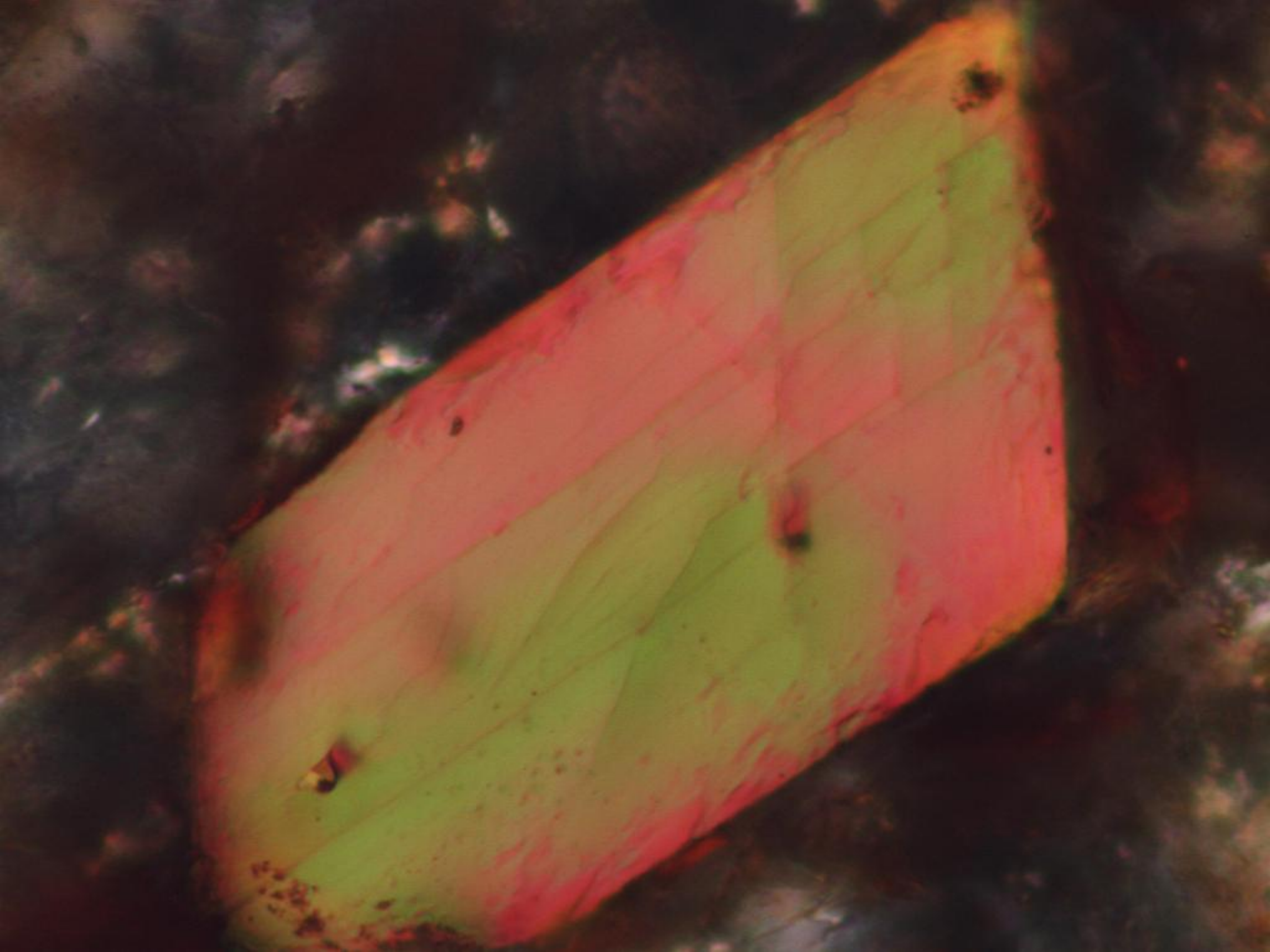
SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS)

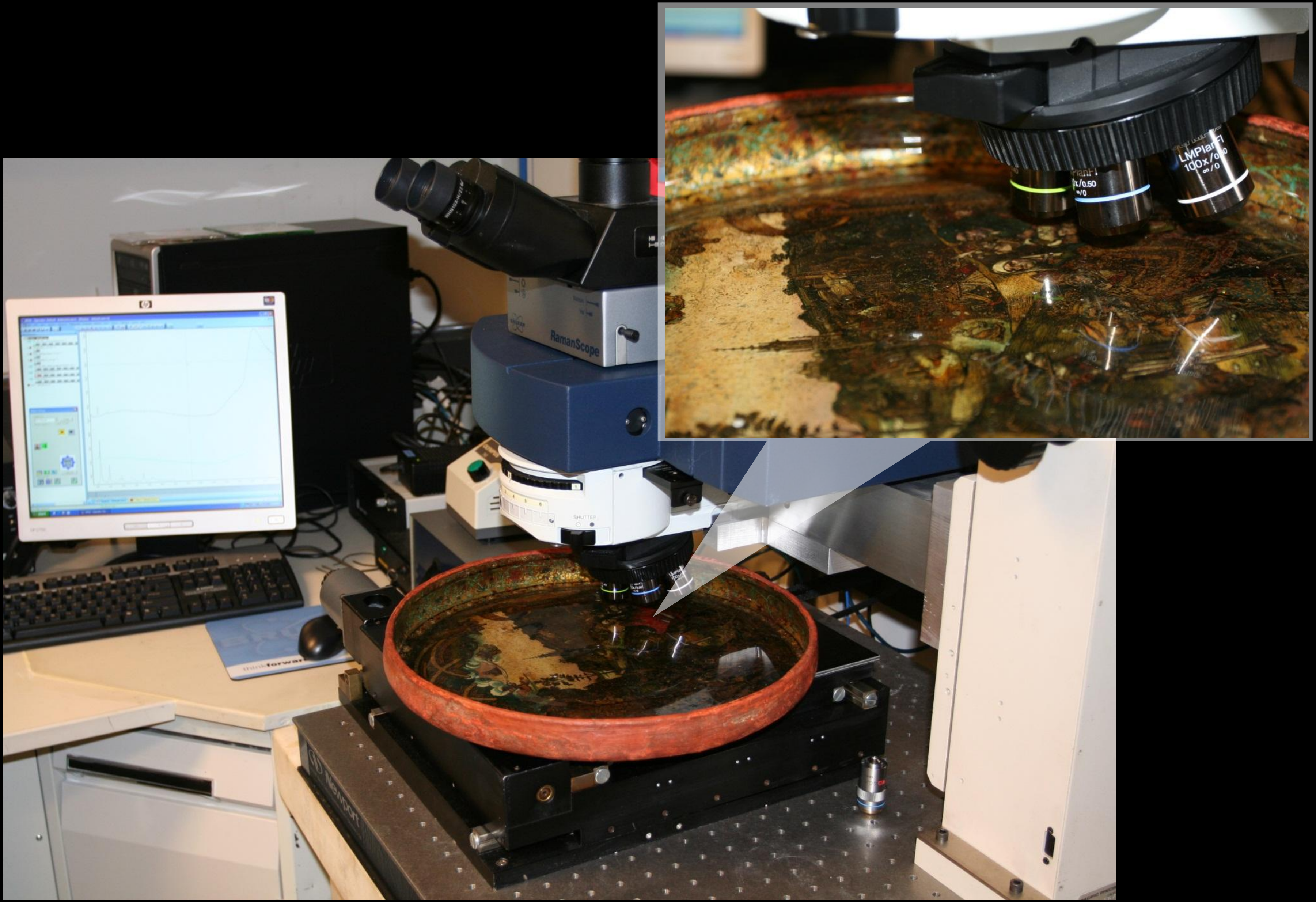




Marco Leona
Department of Scientific Research
The Metropolitan Museum of Art






RamanScope
SHUTTER
LMPlanFl
100x/0.80
∞/0
Newport

RAMAN SCATTERING

ADVANTAGES :

HIGH RESOLUTION SPECTRUM

WATER AS SOLVENT

COUPLING WITH MICROSCOPY TECHNIQUES

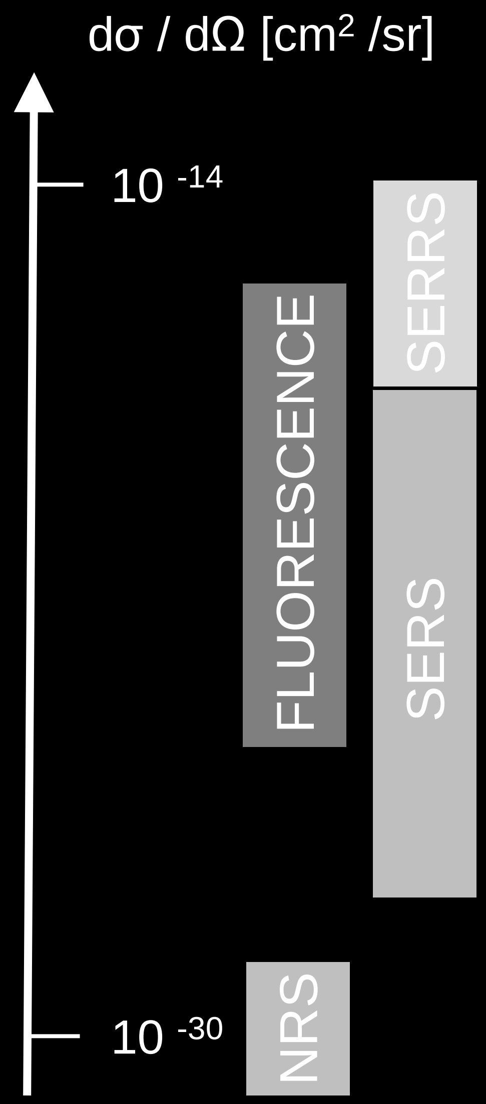
NON-INVASIVE ANALYSIS

CHOICE OF EXCITATION WAVELENGTHS

DISADVANTAGES :

LOW SENSITIVITY

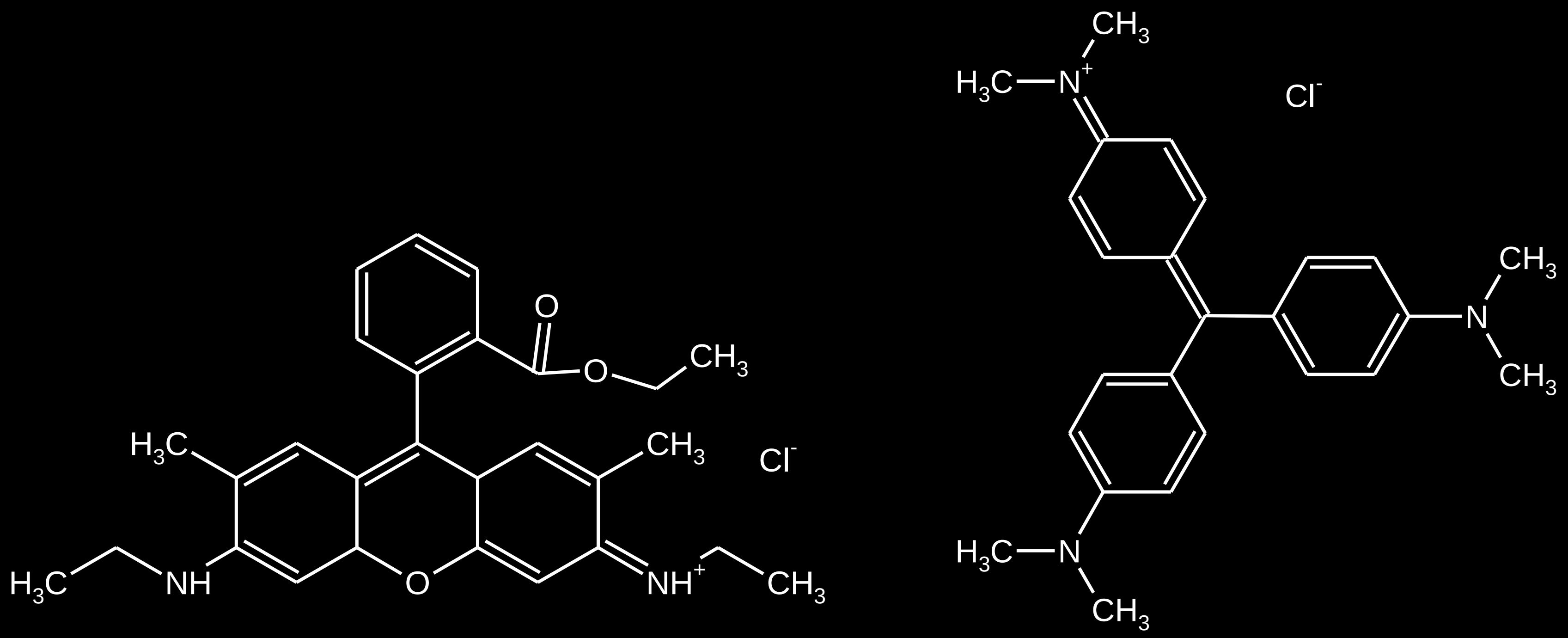
FLUORESCENCE INTERFERENCE



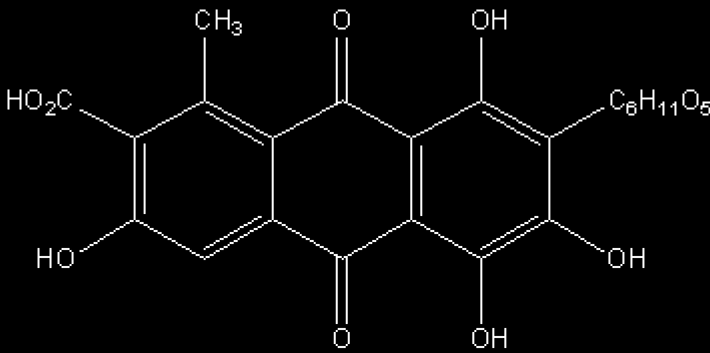
SURFACE ENHANCED RAMAN SCATTERING: GIANT ENHANCEMENT OF RAMAN SCATTERING INTENSITY EXPERIENCED BY MOLECULES ADSORBED ON ATOMICALLY ROUGH METALLIC SURFACES

SINGLE MOLECULE SERS: RHODAMINE 6G AND CRYSTAL VIOLET

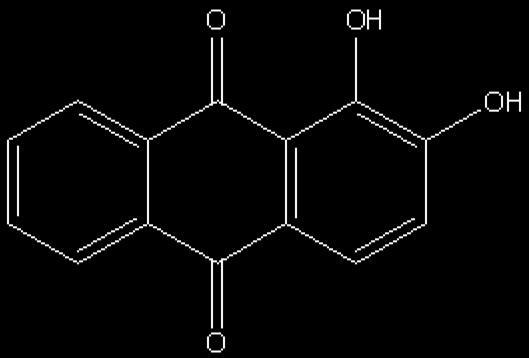
CATIONIC DYES ARE MUCH EASIER TO STUDY WITH SERS (COLLOID BASED SERS) THAN ANIONIC DYES



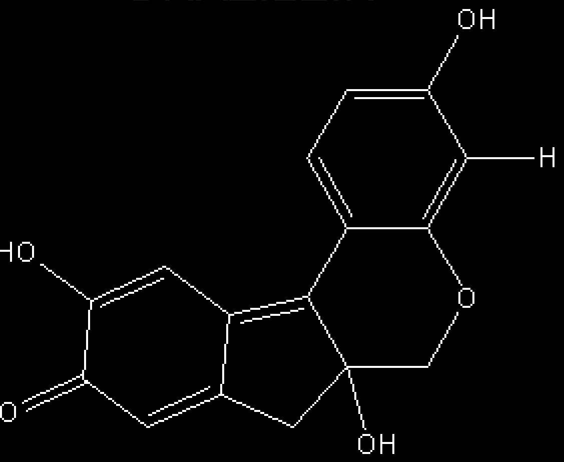
CARMINIC ACID



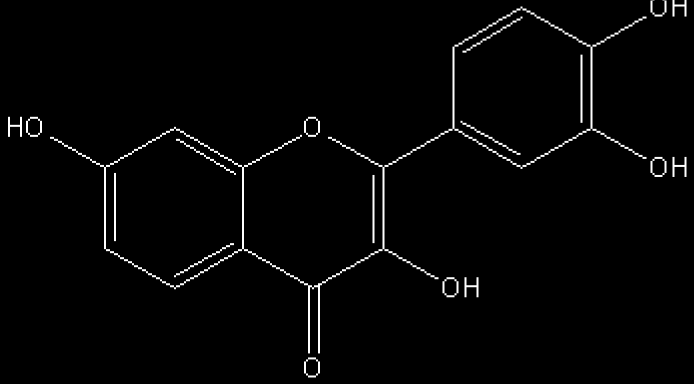
ALIZARIN



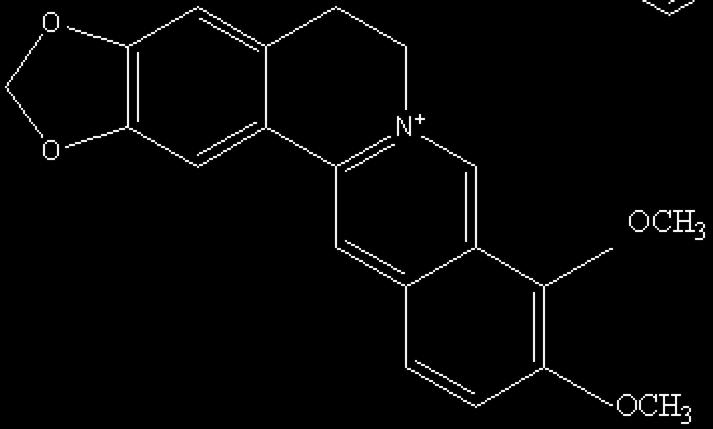
BRAZILEIN



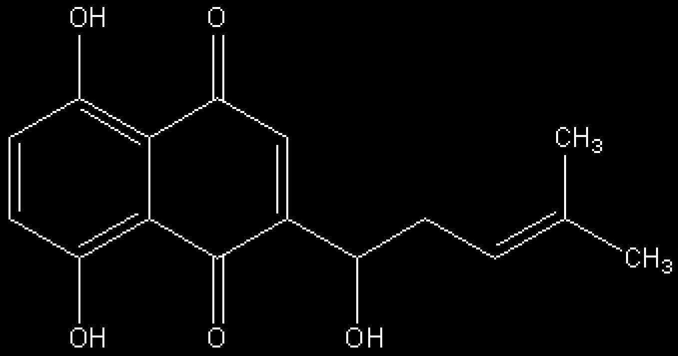
FISETIN



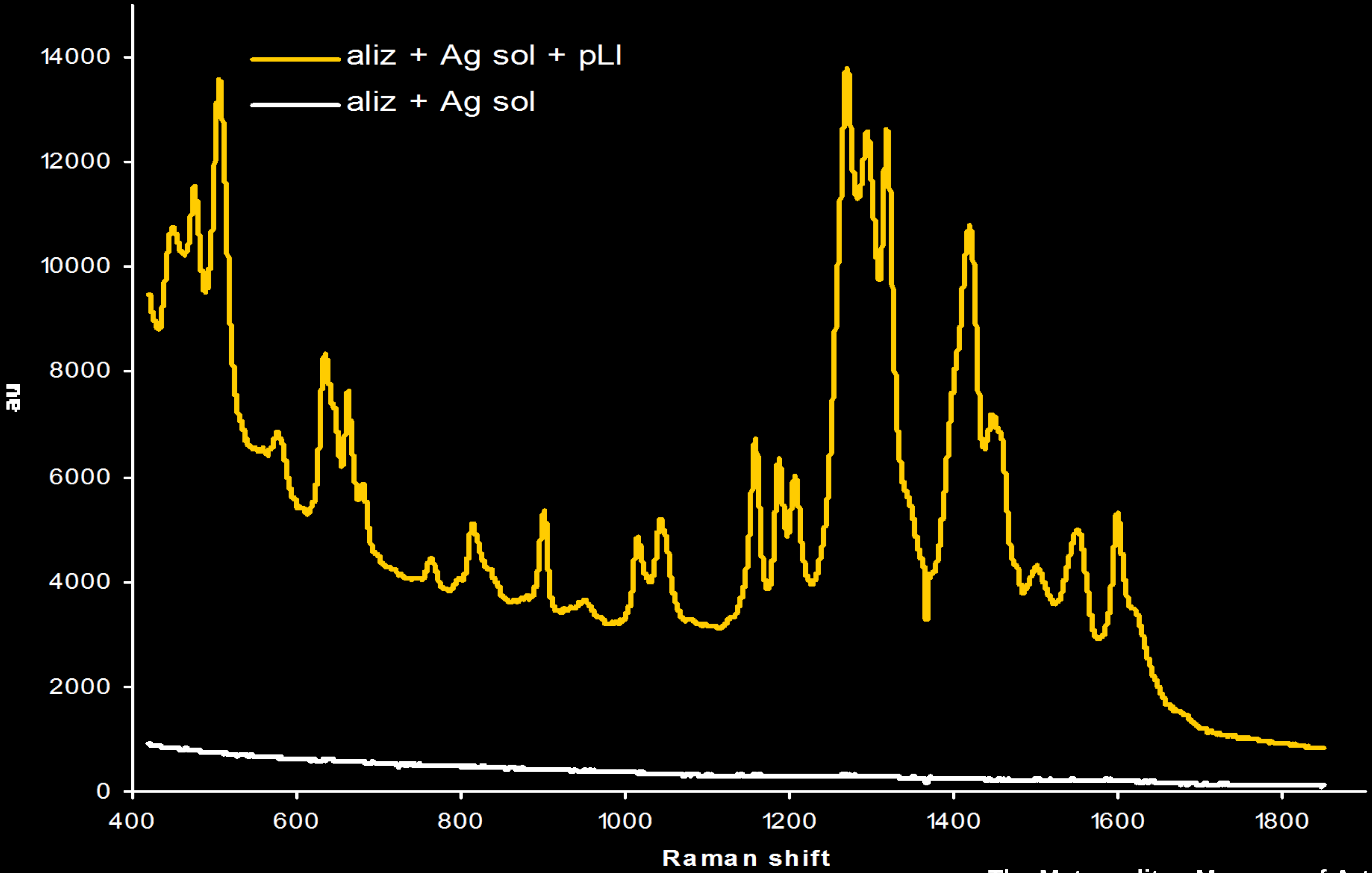
BERBERINE



SHIKONIN/ALKANNIN

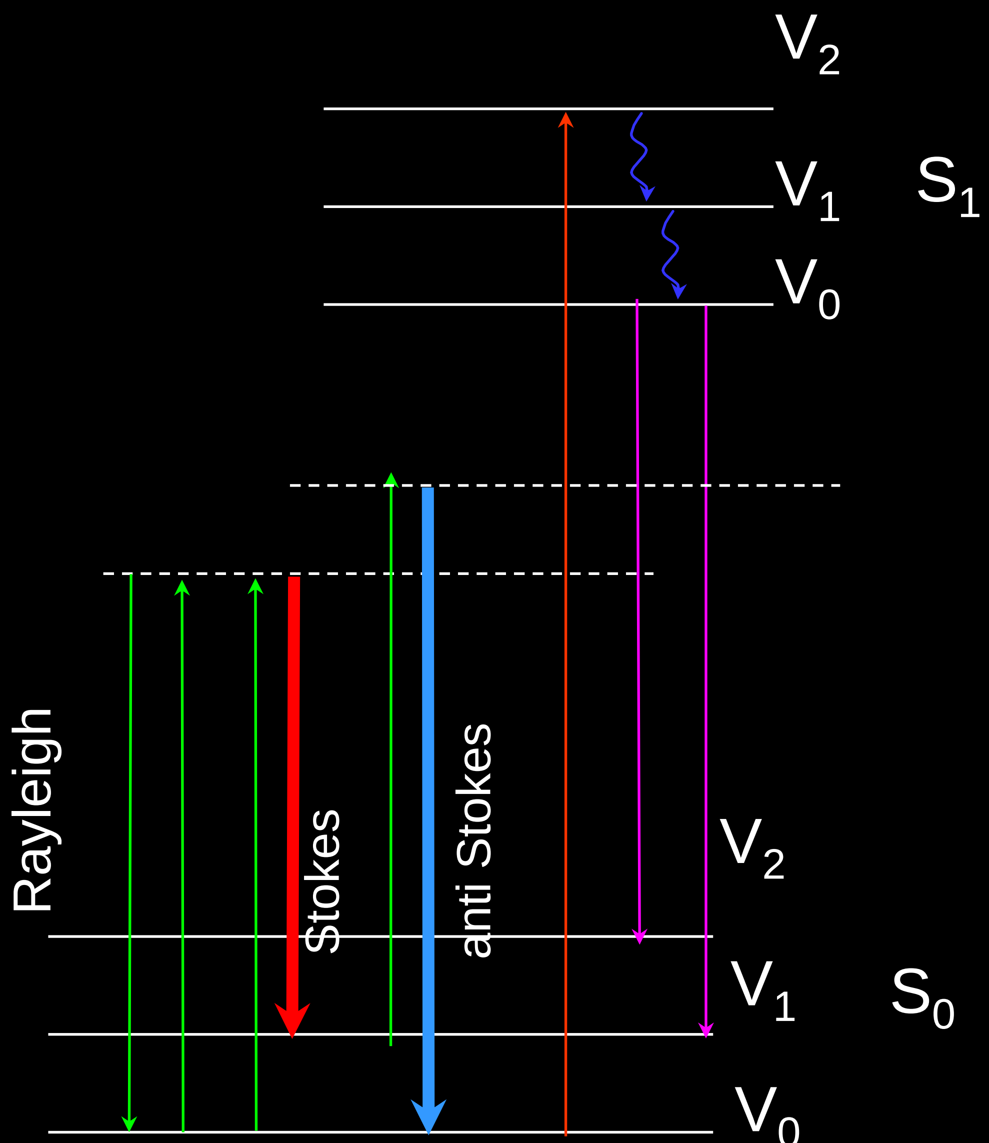


SERS OF ALIZARIN



The Metropolitan Museum of Art

…ALL THE PHYSICS YOU NEED TO KNOW

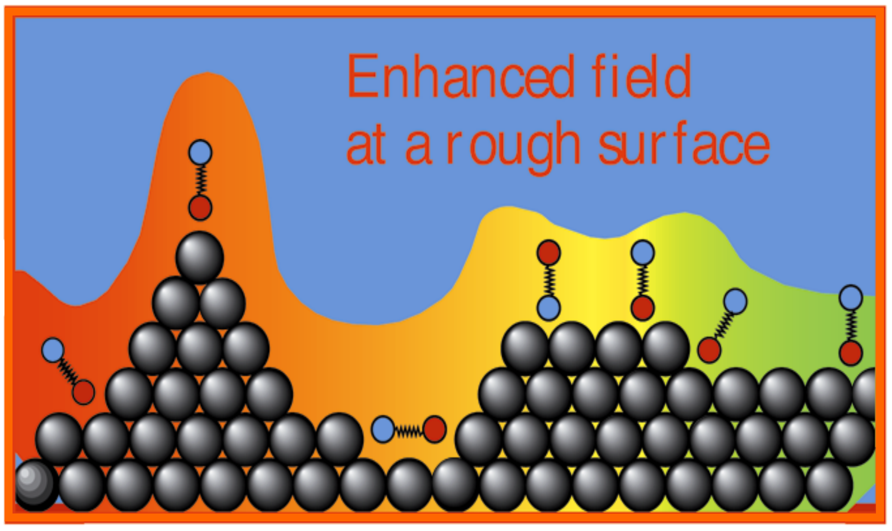


…AND ALL THE MATH YOU NEED TO KNOW

$$R_{IFK}(w) = \frac{m_{KI} m_{FK} h_{IF} \langle i \,|\, Q_k \,|\, f \rangle}{((e_1(w) + 2e_0)^2 + e_2^2)((w_{FK}^2 - w^2) + g_{FK}^2))((w_{IK}^2 - w^2) + g_{IK}^2)}$$

JUST KIDDING…

SURFACE ENHANCED RAMAN SCATTERING (SERS)



Surface enhancement factor:

Rough surface 10^2~10^6

Single molecule > 10^{12} (10^{14})

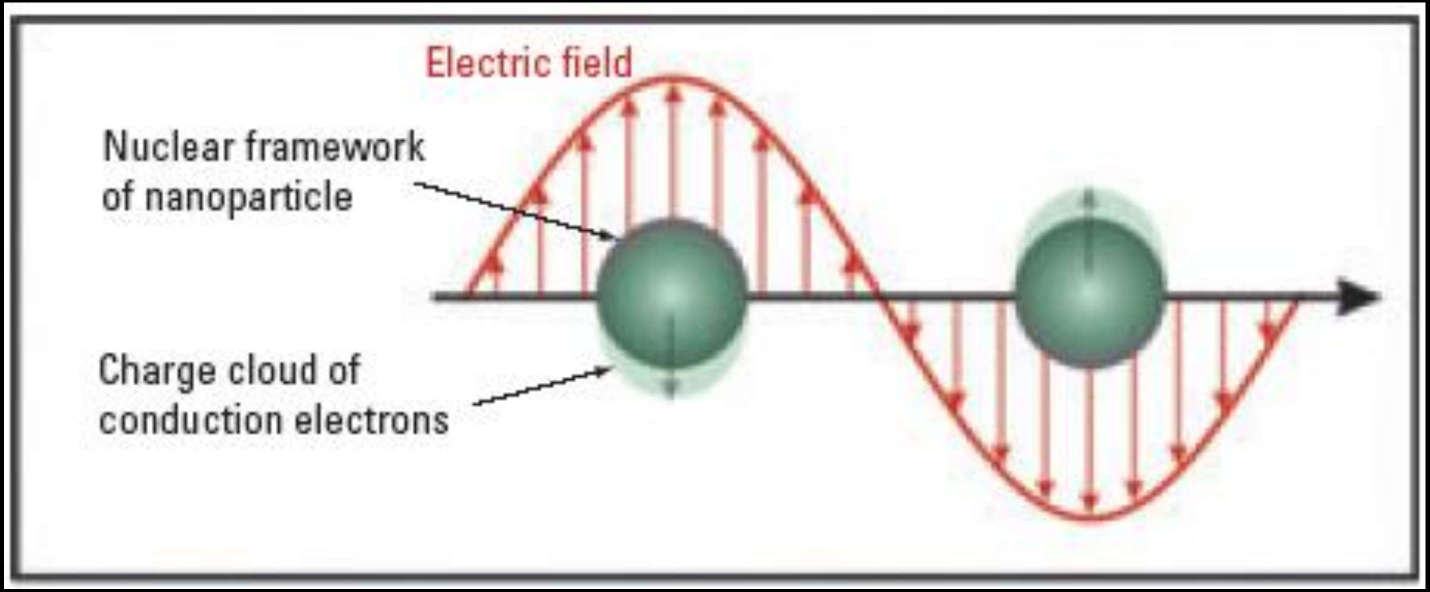
Atomically rough metallic substrates (nanostructure is necessary).

Only Ag, Cu, Au can give rise to strong SERS at the common Raman excitation wavelengths

Local electric field is enhanced (Local Surface Plasmon Resonance).

SURFACE PLASMON RESONANCE

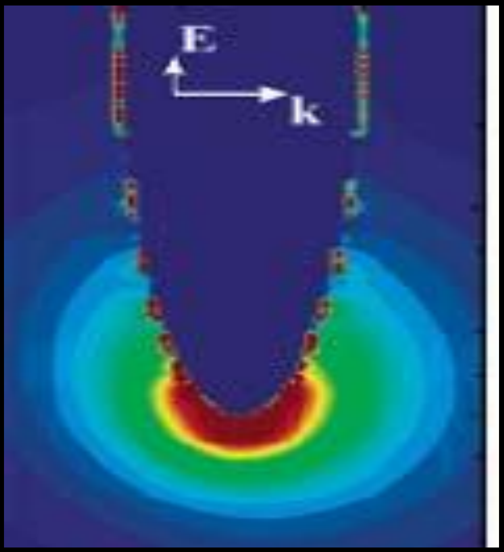
When electromagnetic radiation with the same frequency is incident upon the nanostructure, the electric field of the radiation drives the conduction electrons into collective oscillation.
Excitation of the SPR has two consequences: selective absorption and scattering of the resonant electromagnetic radiation, and generation of large electromagnetic fields at surface of roughness.

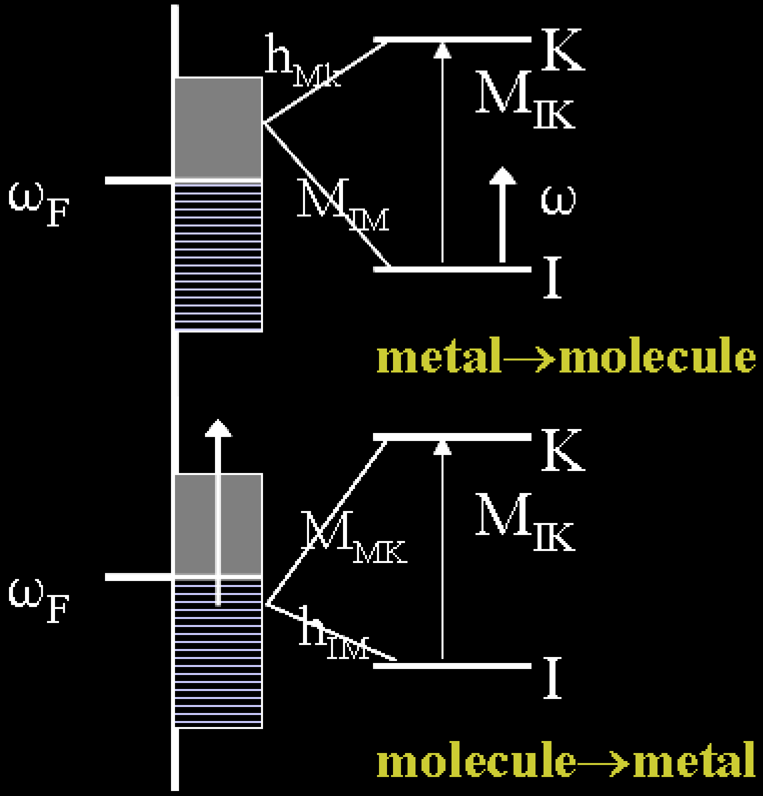


SURFACE ENHANCEMENT MECHANISM AND MAGNITUDE

$$I = \alpha^2 \cdot E^2 \approx 10^6$$

Electromagnetic enhancement
related to the distance between the absorbate and the metal surface



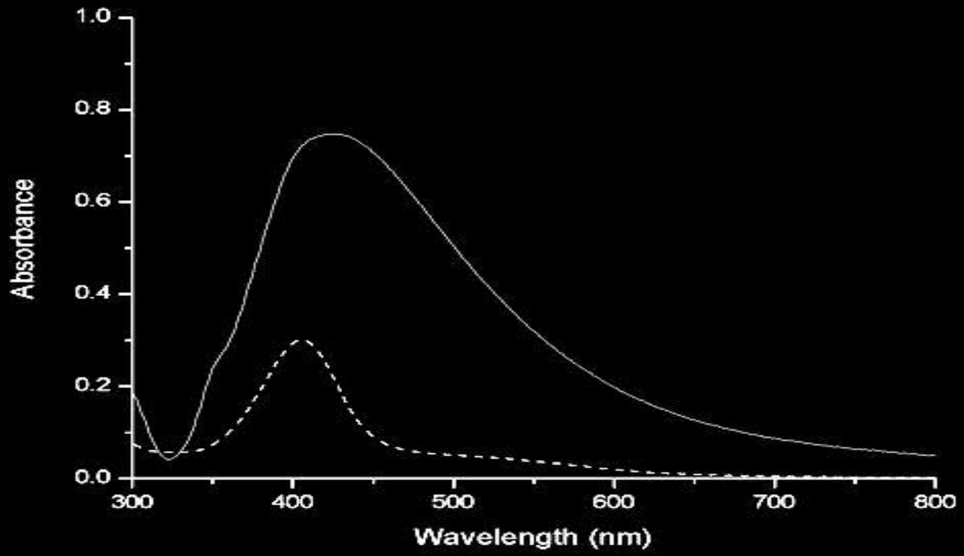


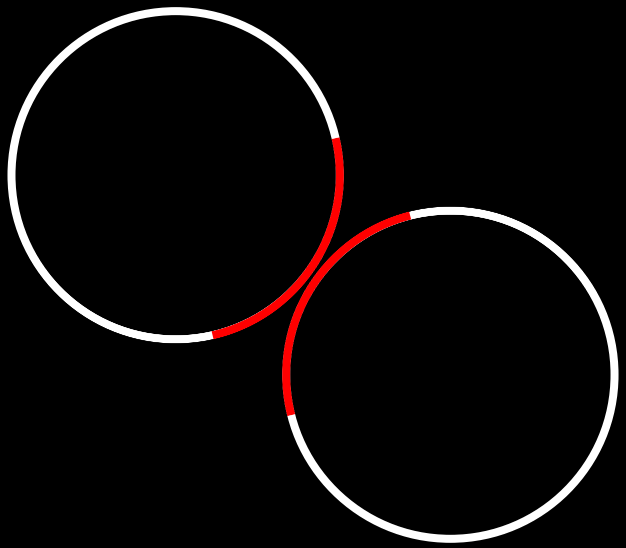
Chemical enhancement
related with the chemical bond between the adsorbate and the metal atom

SURFACE ENHANCED RAMAN SCATTERING SUPPORTS

The Metropolitan Museum of Art

SURFACE ENHANCED RESONANCE RAMAN SPECTROSCOPY ON SILVER COLLOIDS





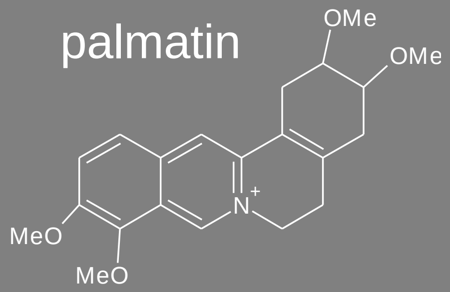
BROAD PLASMONIC RESONANCE
HIGHER ENHANCEMENT DUE TO AGGREGATION AND HOT SPOTS FORMATION
ENSEMBLE AVERAGED SERS vs SINGLE MOLECULE
COMPLICATIONS ARISING FROM SURFACE CHEMISTRY
DISPLACEMENT – COADSORPTION – PREFERENTIAL ADSORPTION
LIMITED TO WATER SOLUBLE ANALYTES

SERS SPECTRA AND ORDINARY RAMAN SPECTRA

RAMAN AND SERS: ISOQUINOLINE ALKALOIDS

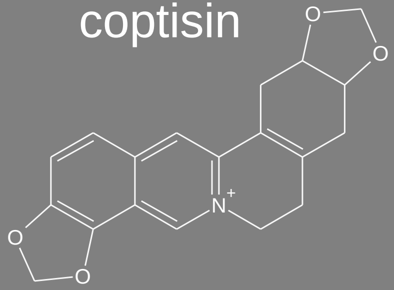
berberin

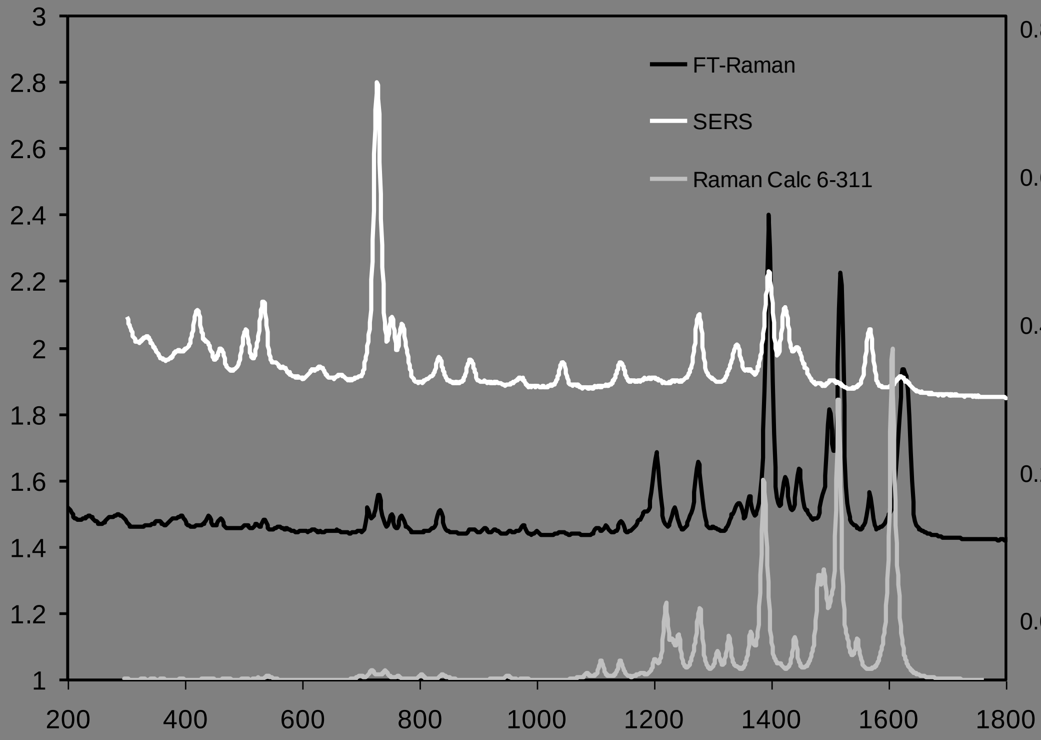
palmatin

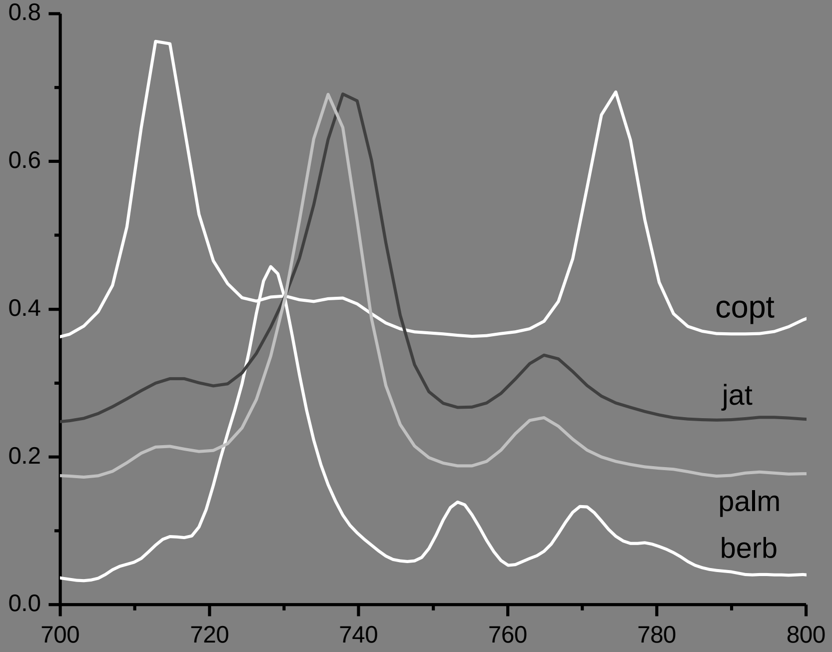


jatrorrhizin

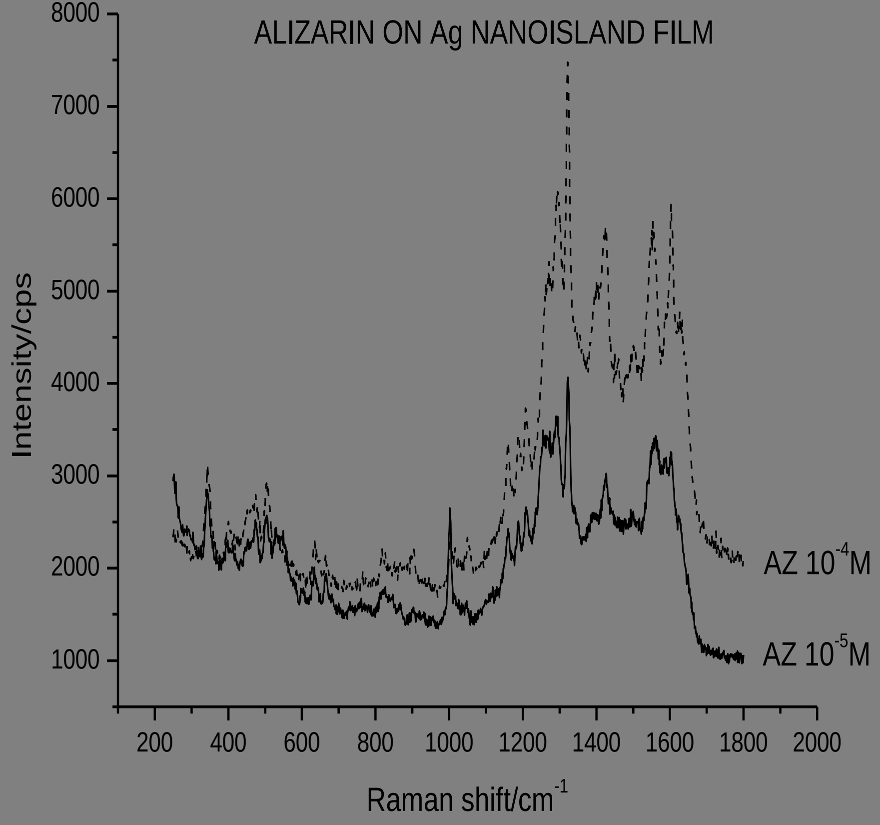
coptisin

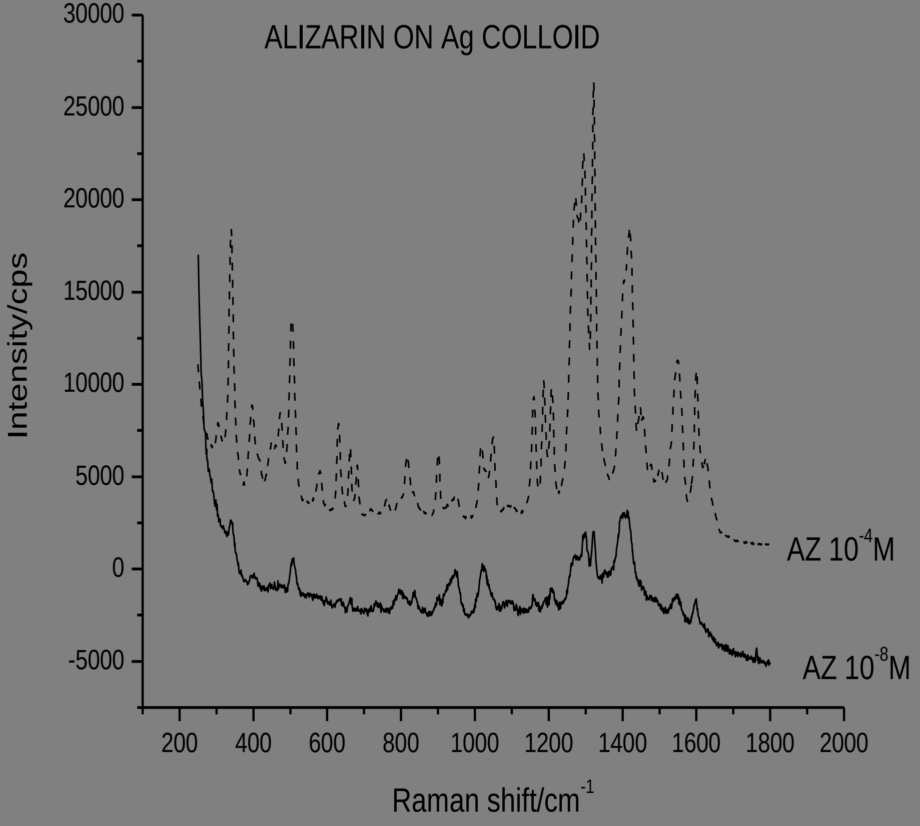






LOD: COLLOIDS AND NANOISLAND FILMS





SERS IS AN IDEAL TECHNIQUE FOR THE ANALYSIS OF ORGANIC COLORANTS (BUT IT ISN'T A SEPARATION TECHNIQUE IN THE ANALYTICAL SENSE – HPLC OR LCMS PREFERRED IF ENOUGH SAMPLE IS AVAILABLE)

SERS HAS BECOME AN ESTABLISHED TECHNIQUE IN THE ANALYSIS OF ARTISTIC AND ARCHAEOLOGICAL MATERIAL (MORE THAN 100 OBJECTS STUDIED BY SERS AT MMA)

PROBLEMS PREVENTING BROADER ANALYTICAL USE OF SERS:

PERCEIVED LACK OF REPRODUCIBILITY
SMALL NUMBER OF COMPOUNDS STUDIED SO FAR
LARGE DIFFERENCES IN SERS EFFICIENCY EVEN FOR CLOSELY RELATED COMPOUNDS
LACK OF SEARCHABLE DATABASES
INTERFERENCES DUE TO IMPURITIES OR MATRIX COMPONENTS

AND FINALLY, SERS STILL REQUIRES REMOVING A SAMPLE –HOWEVER MICROSCOPIC- FROM THE OBJECT UNDER ANALYSIS.

SERS ANALYIS IN THE ARTS AND IN THE FORENSIC FIELD IS SIGNIFICANTLY DIFFERENT THAN IN THE BIOMEDICAL OR ENVIRONMENTAL ANALYSIS FIELD

ONE MICROSCAMPLE (<100 μm DIAMETER) IN WHICH THE TARGET ANALYTE IS AT LESS THAN 5% CONCENTRATION (DYES IN THESE SAMPLES CANNOT BE DETECTED BY IR SPECTROSCOPY)

MICRO TOTAL ANALYSIS (μTAS) + TRACE ANALYSIS

MATRIX INTERFERENCES (SUBSTRATE, BINDERS, SOIL, DEGRADATION PRODUCTS, BIOLOGICAL GROWTH) AND COMPETITION FOR ADSORPTION ON PLASMONIC SUPPORTS FROM RELATED COMPOUNDS (DYES IN MIXTURES) MUST BE TAKEN INTO ACCOUNT

SURFACE CHEMISTRY IS GENERALLY IGNORED BY MOST SERS RESEARCHERS, WHILE IT IS THE SINGLE MOST IMPORTANT FACTOR IN DETERMINING ENHANCEMENT (ie: NO ADSORPTION, NO SERS)

MICROSAMPLING

PRE-TREATMENT OF SAMPLE WITH A “ONE-POT” REACTION TO MAXIMIZE DYE ADSORPTION ON COLLOID AND MINIMIZE LOSSES

EASILY AND REPRODUCIBLY SYNTHESIZED MONODISPERSE COLLOID: MICROWAVE SUPPORTED GLUCOSE REDUCTION OF SILVER SULFATE IN PRESENCE OF SODIUM CITRATE

RESONANT EXCITATION

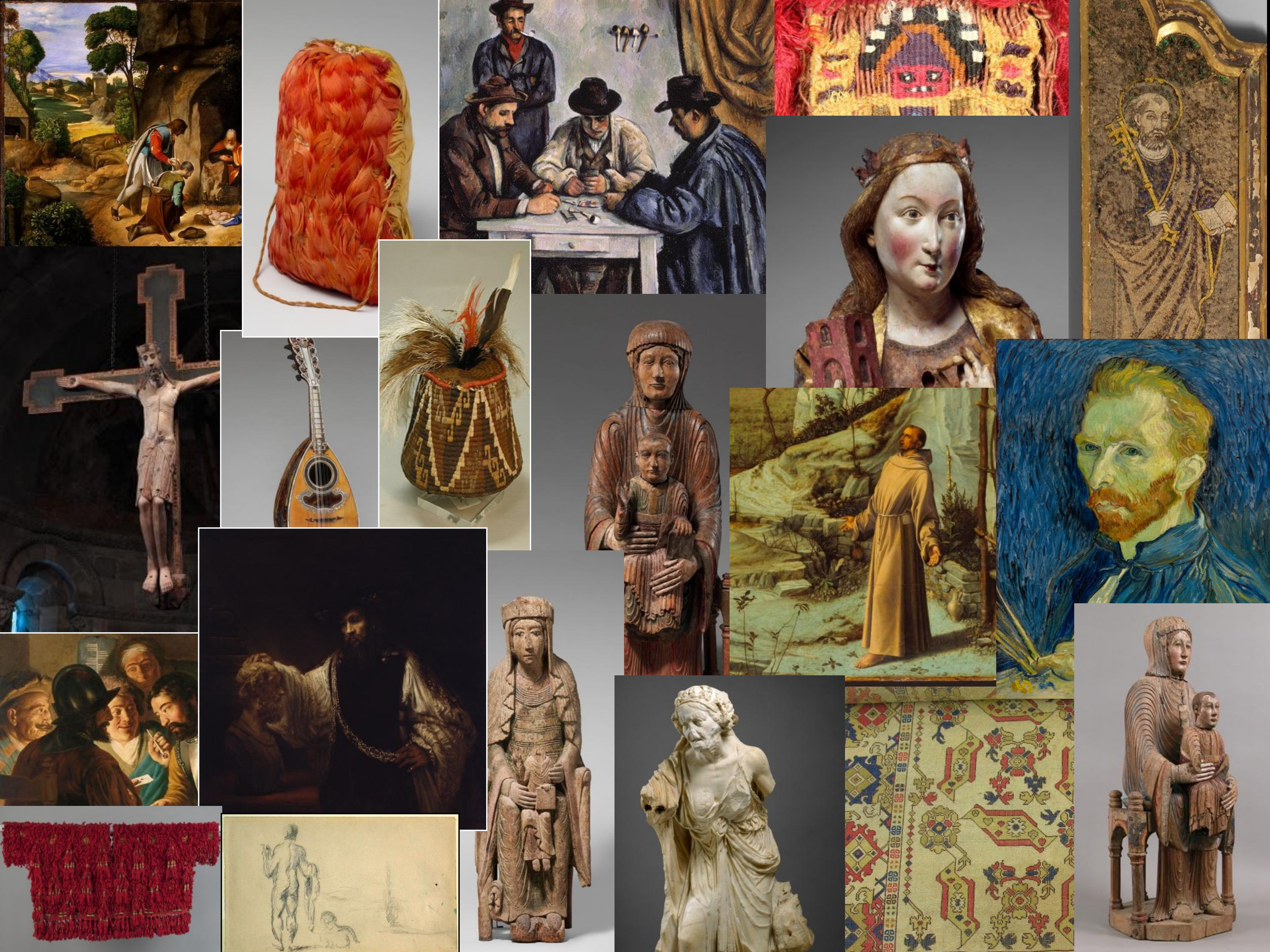
SERS SPECTRAL LIBRARY (DYES AND CONTROLLED SUBSTANCES)

STANDARDIZED COLLOID DELIVERY BY PIEZOELECTRIC INKJET

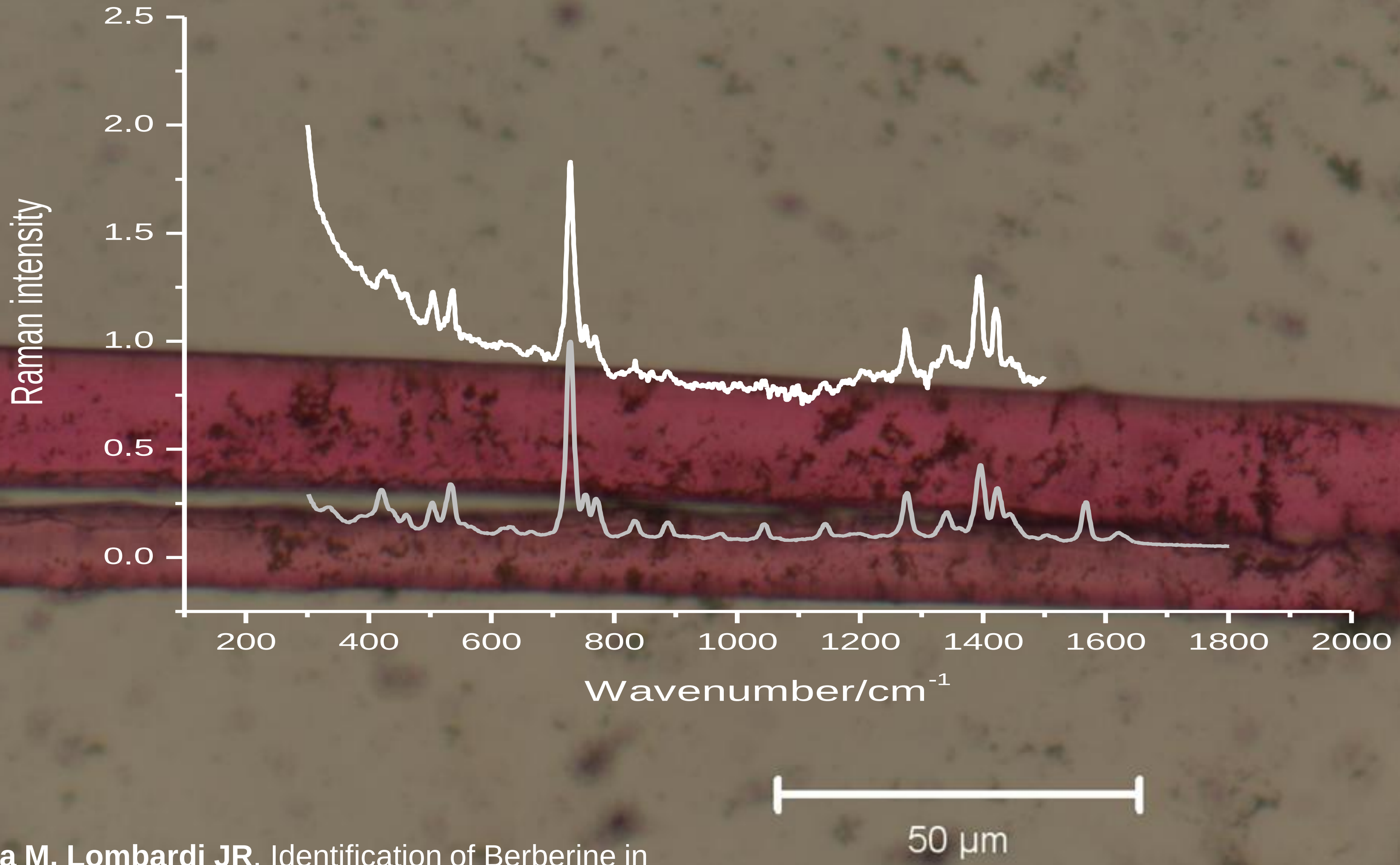
HYDROGEL MICROEXTRACTION

TUNABLE EXCITATION (OPO SYSTEM)

CASE STUDIES (… THE SERS MUSEUM OF ART)

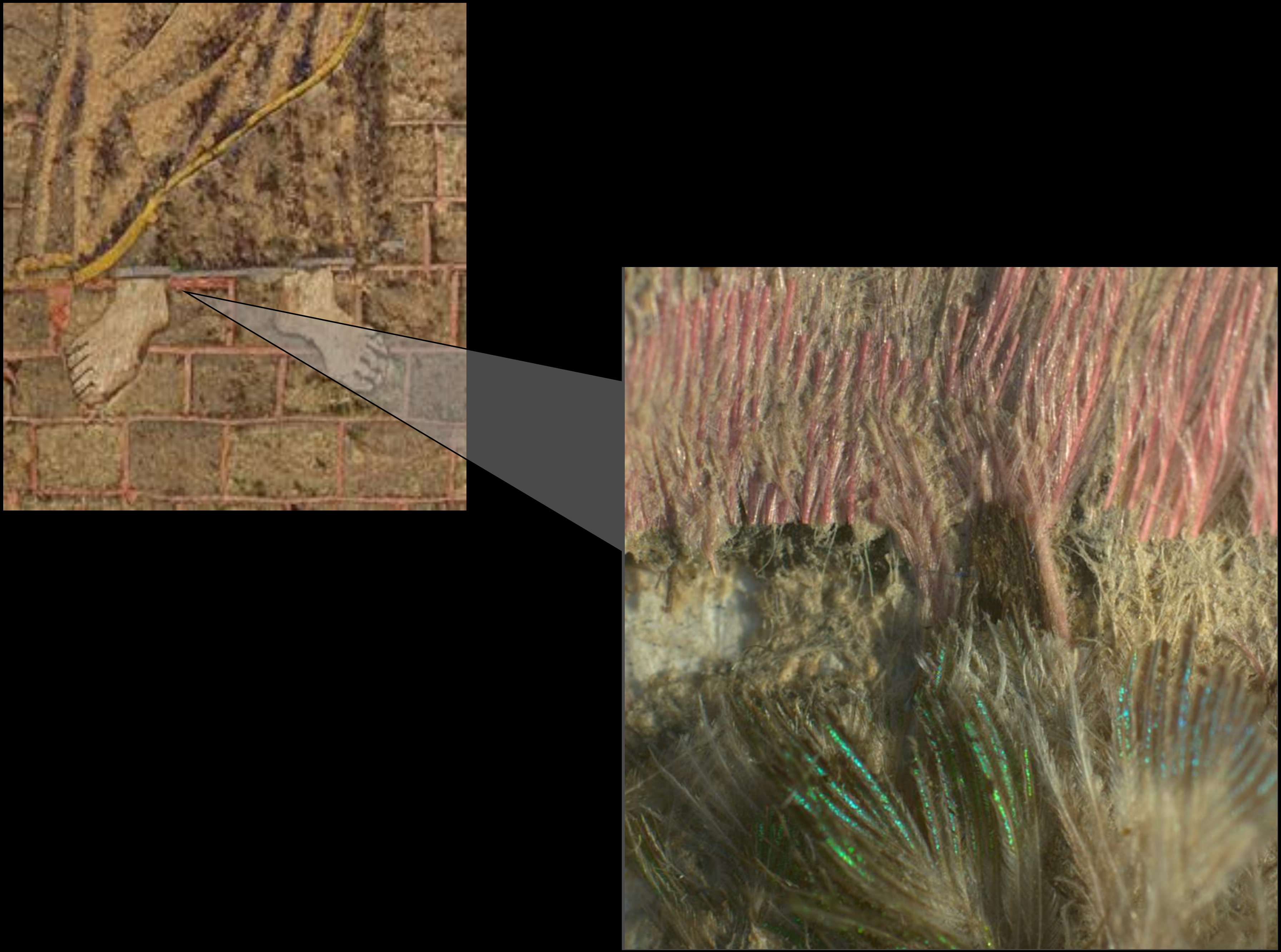


SINGLE FIBER ANALYSIS WITH HF PRETREATMENT



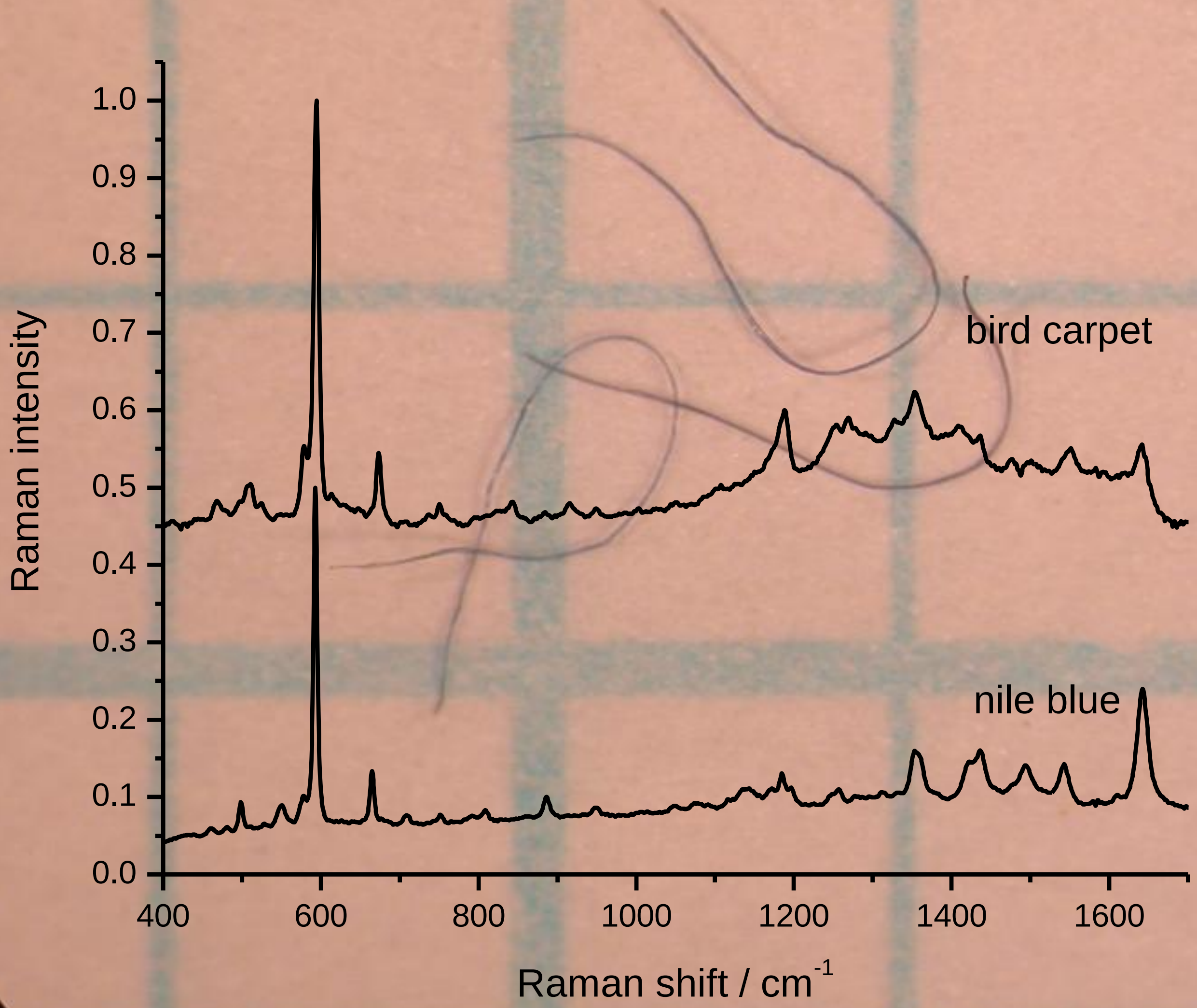
Leona M, Lombardi JR. Identification of Berberine in Archaeological Textiles by Surface Enhanced Raman Spectroscopy. *J. Raman Spectrosc.* 2007; **38**: 853-858


Hoc est enim corpus meum
Hic est enim calix sanguinis
mei novi et eterni testamenti
mysterium fidei: qui pro vobis
et pro multis effundetur in re
missionem peccatorum

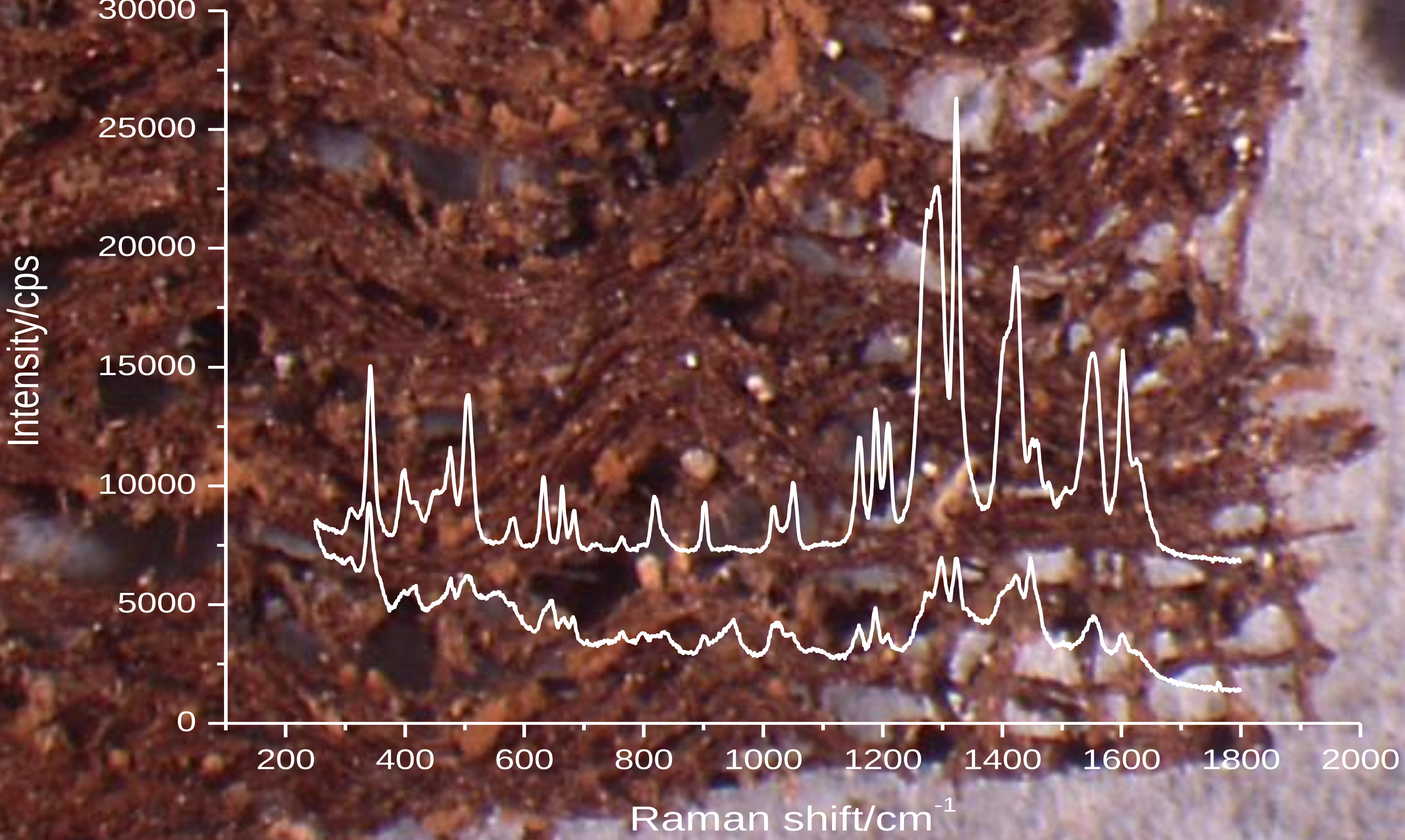


The Metropolitan Museum of Art

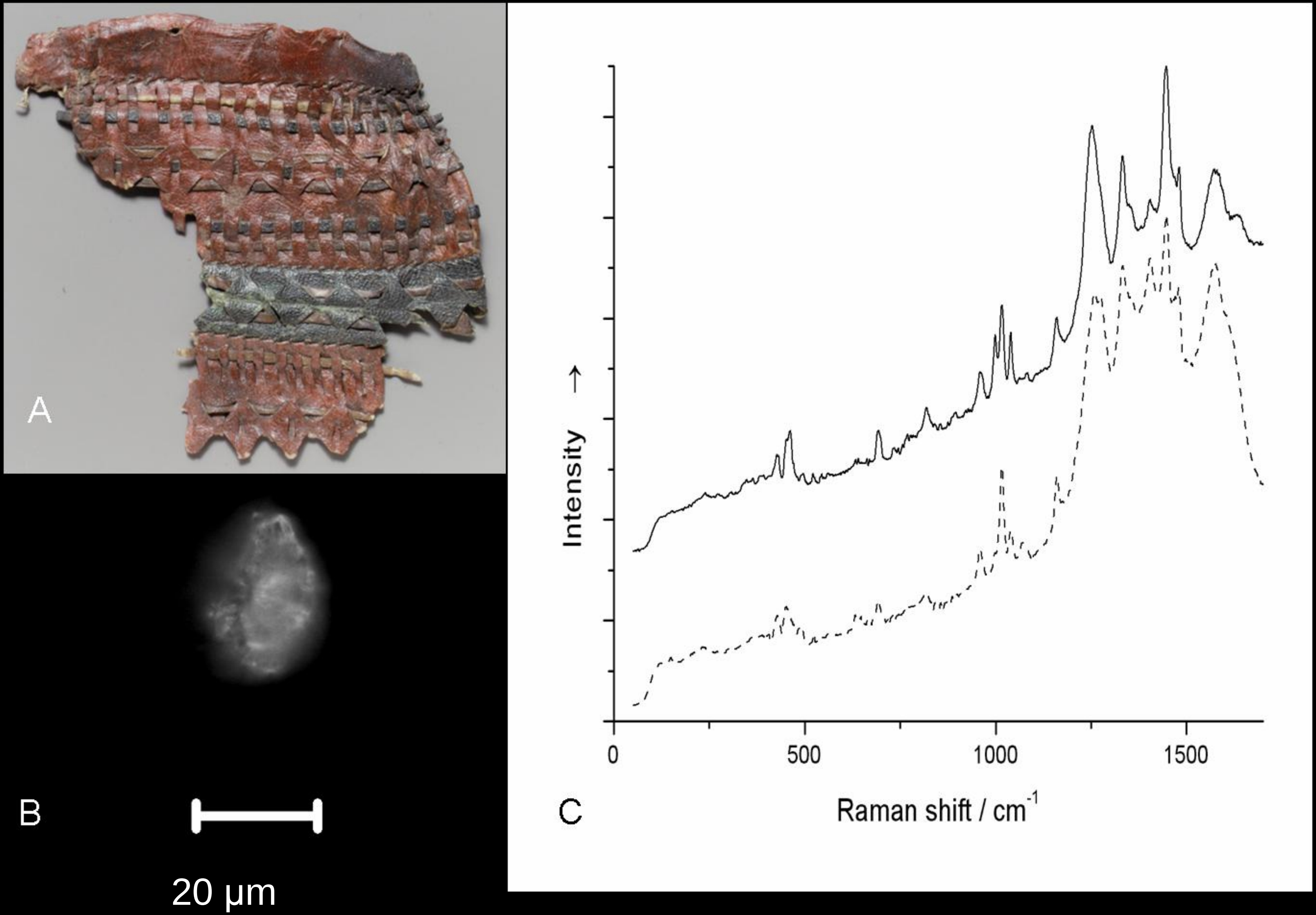
MINIMAL SAMPLE SIZE!



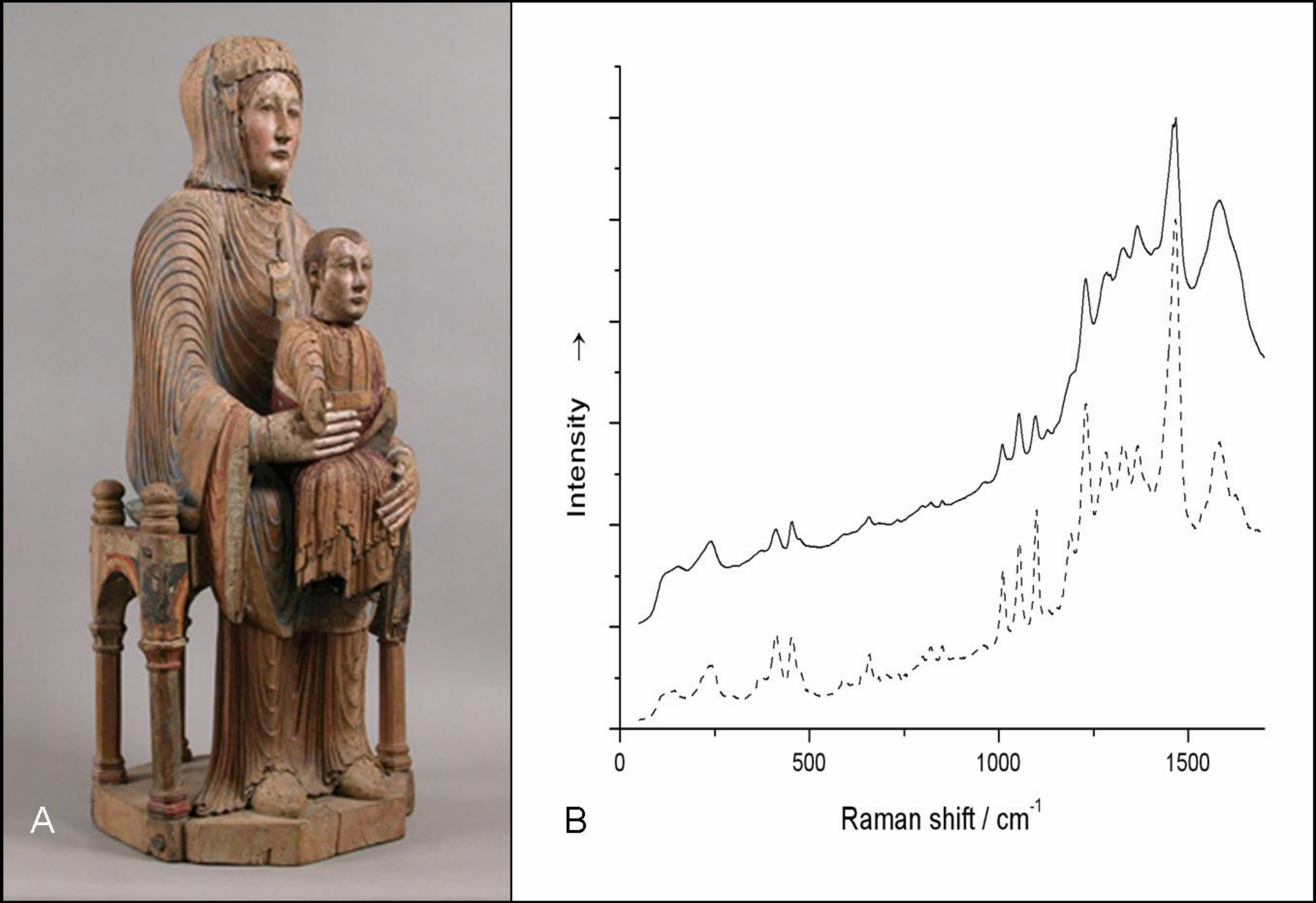
AN 11TH C TEXTILE FRAGMENT

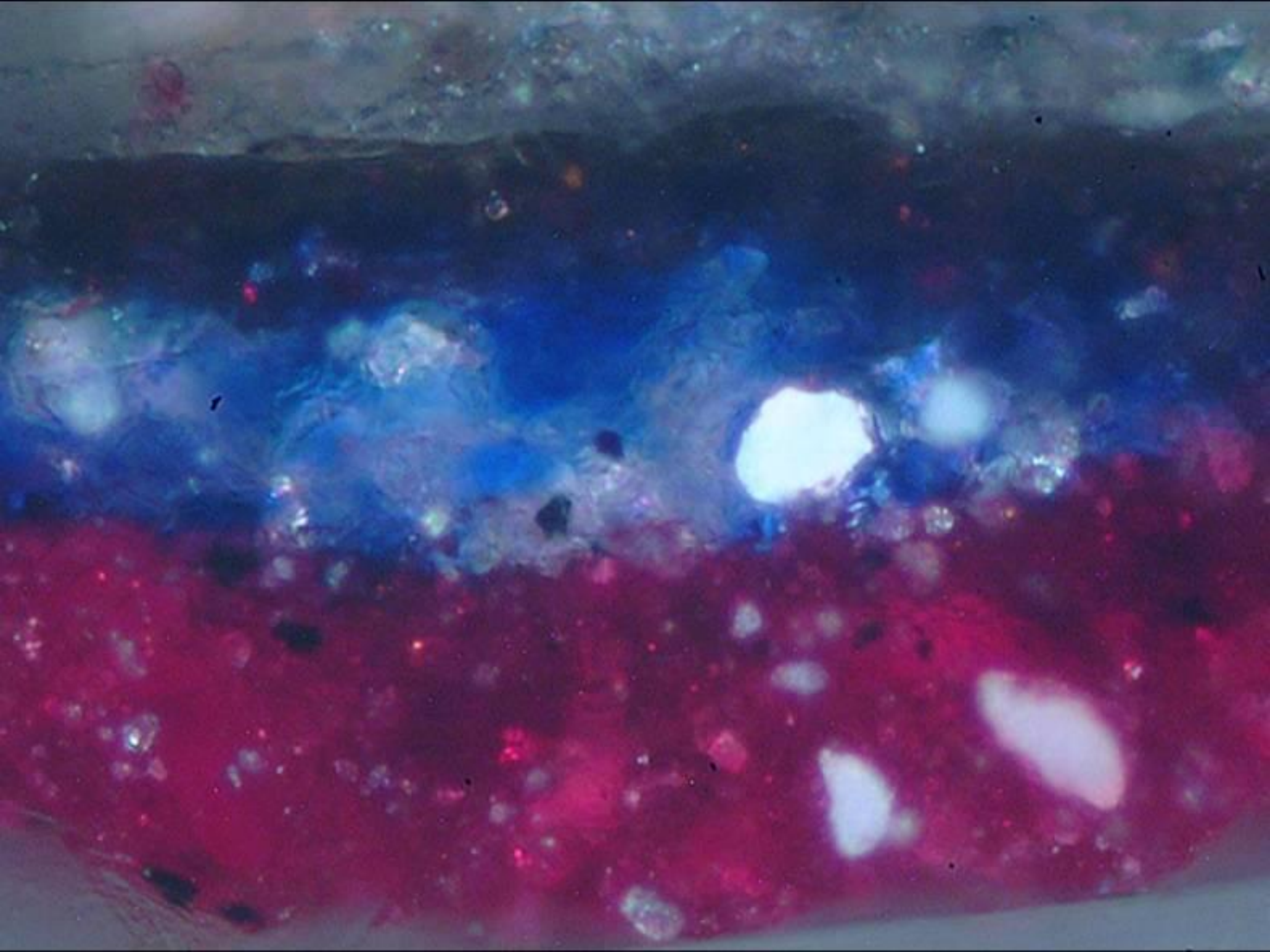


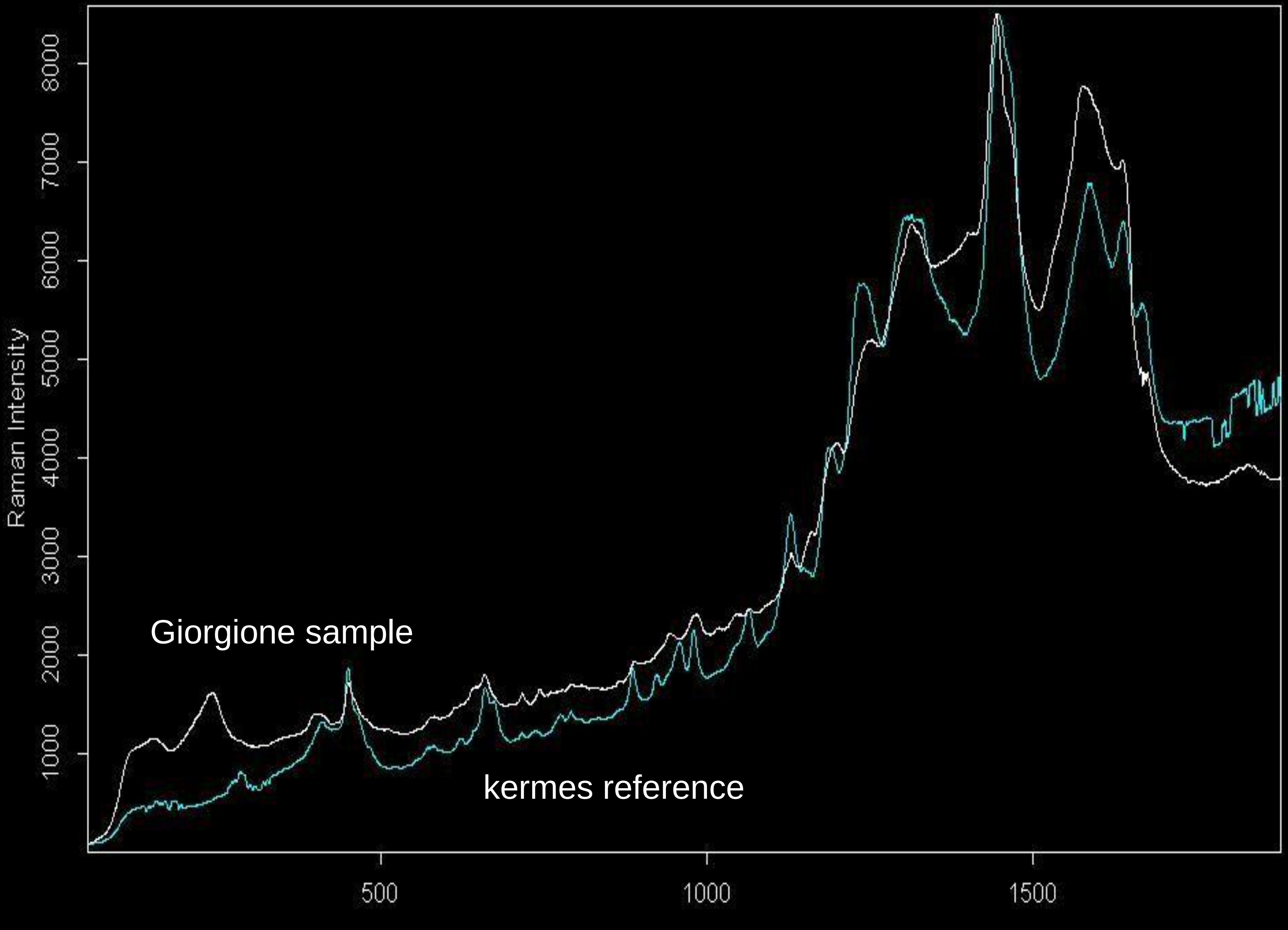
The Metropolitan Museum of Art

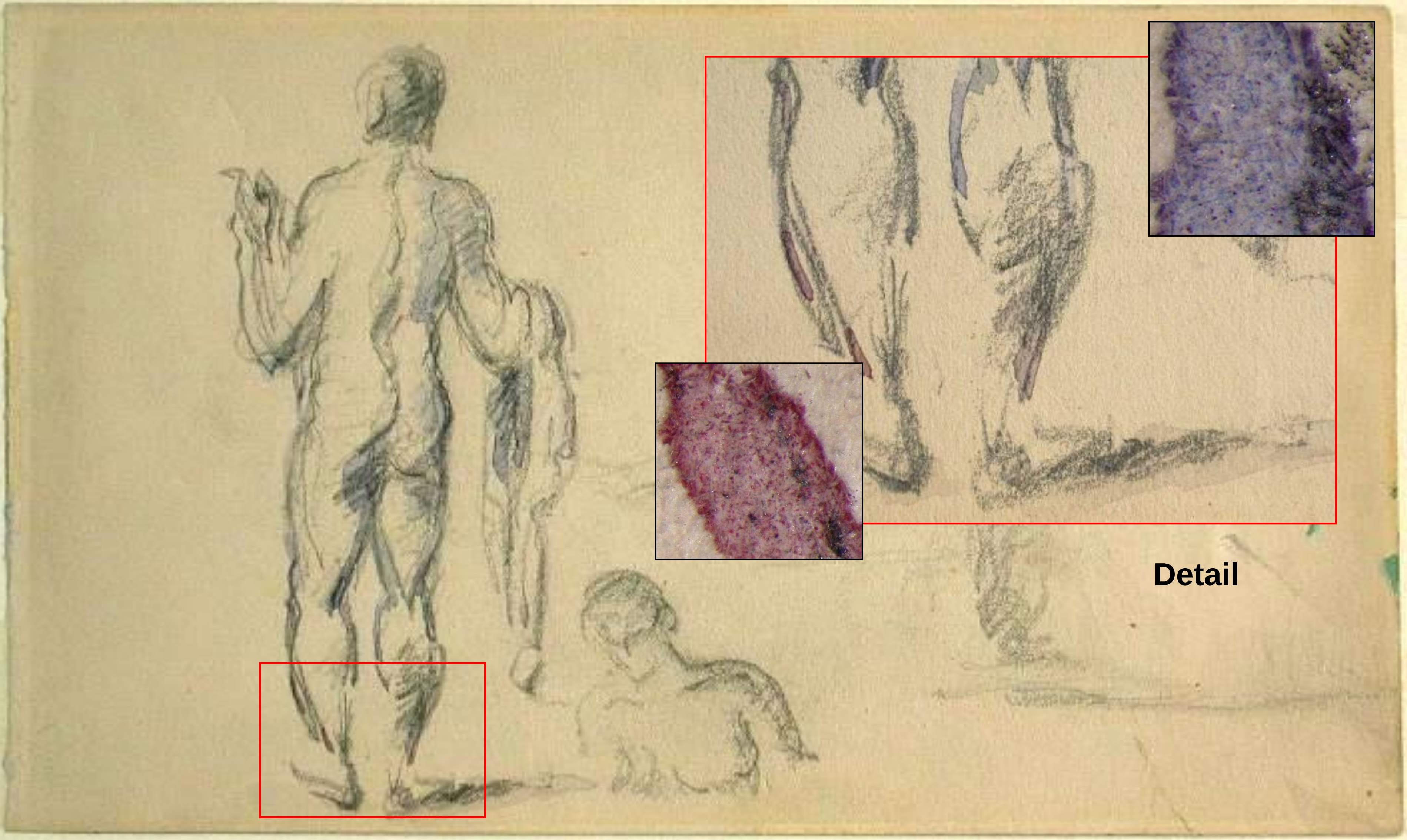


Leona, M. Microanalysis of organic pigments and glazes in polychrome works of art by surface-enhanced resonance Raman scattering. *PNAS.* 2009, **106**, 14757-14762

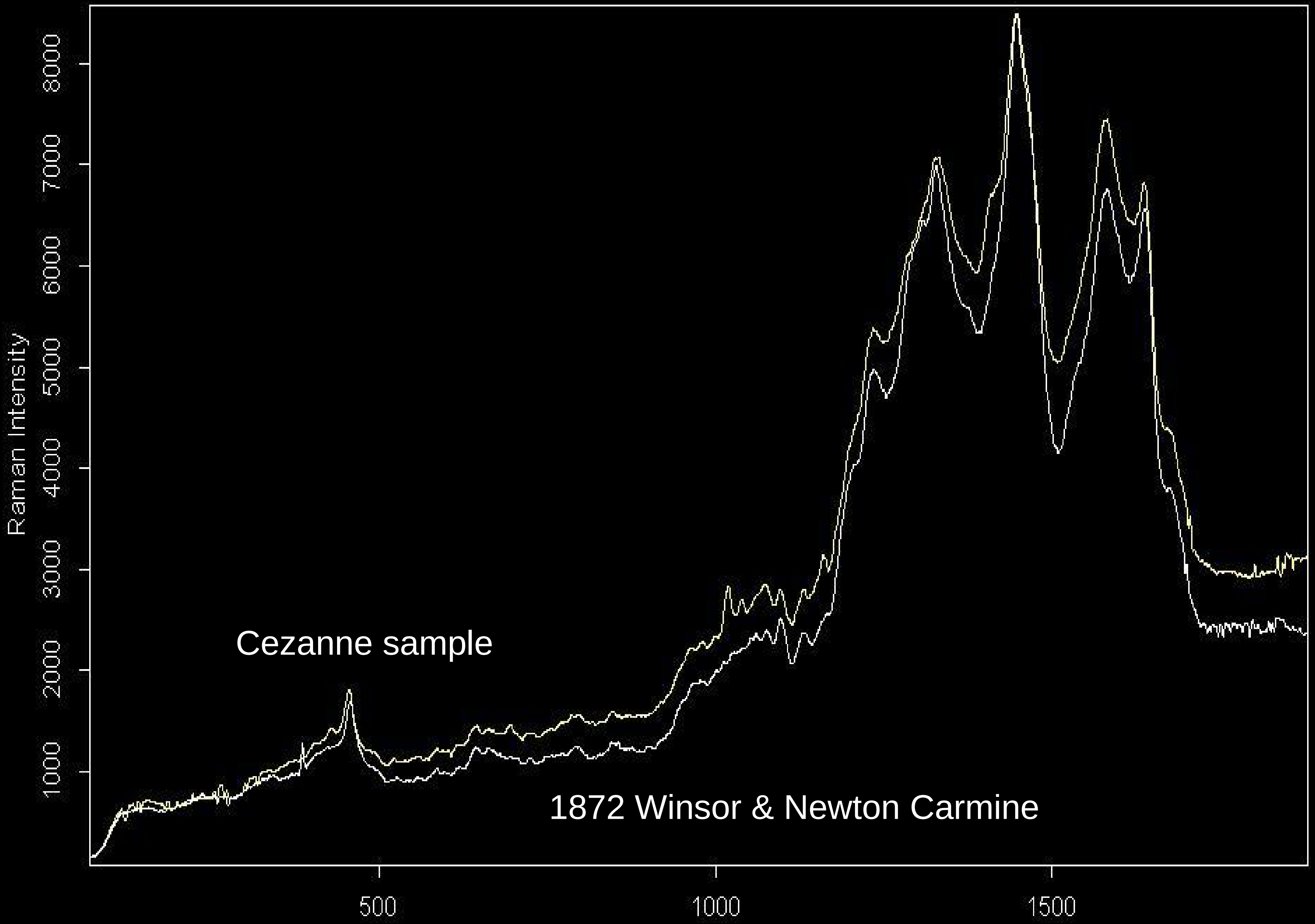

A
B
Intensity →
0
500
1000
1500
Raman shift / cm-1

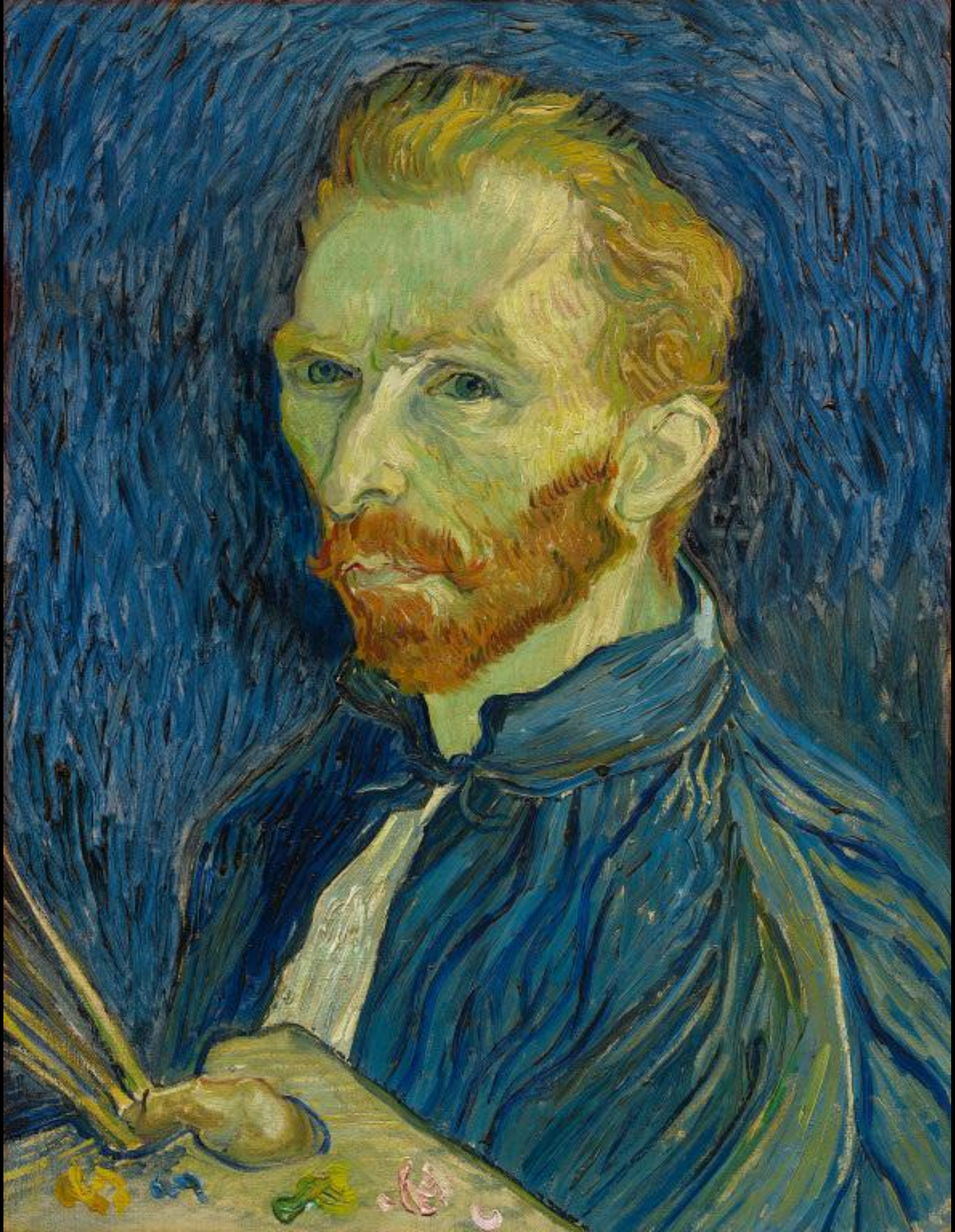



Giorgione sample
kermes reference
Raman Intensity
1000
2000
3000
4000
5000
6000
7000
8000
500
1000
1500



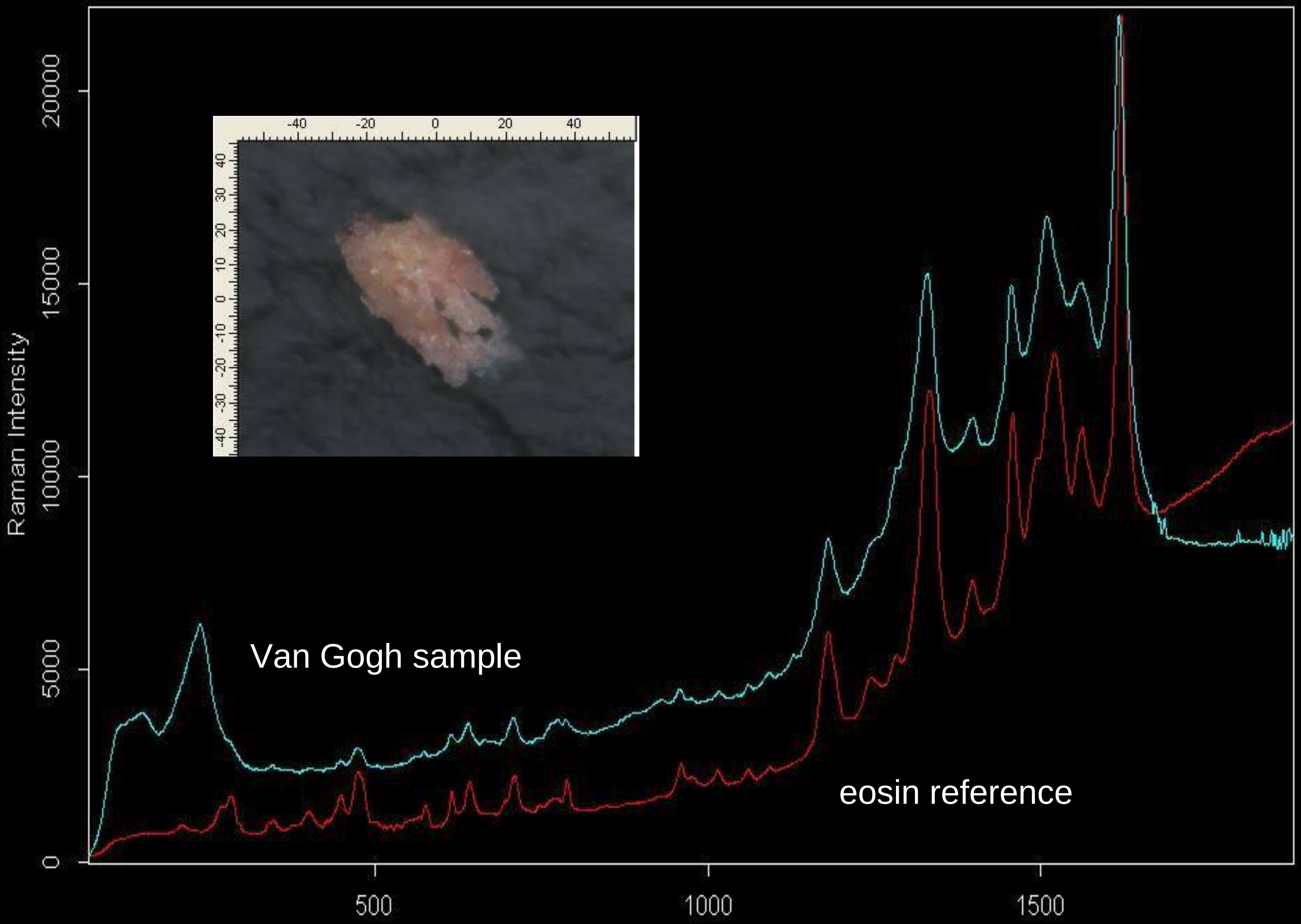
TWO MALE BATHERS; CEZANNE SKETCHBOOK II, C. 1885-1900
PHILADELPHIA MUSEUM OF ART, ACC# 1987-53-62B


Raman Intensity
8000
7000
6000
5000
4000
3000
2000
1000
500
1000
1500
Cezanne sample
1872 Winsor & Newton Carmine

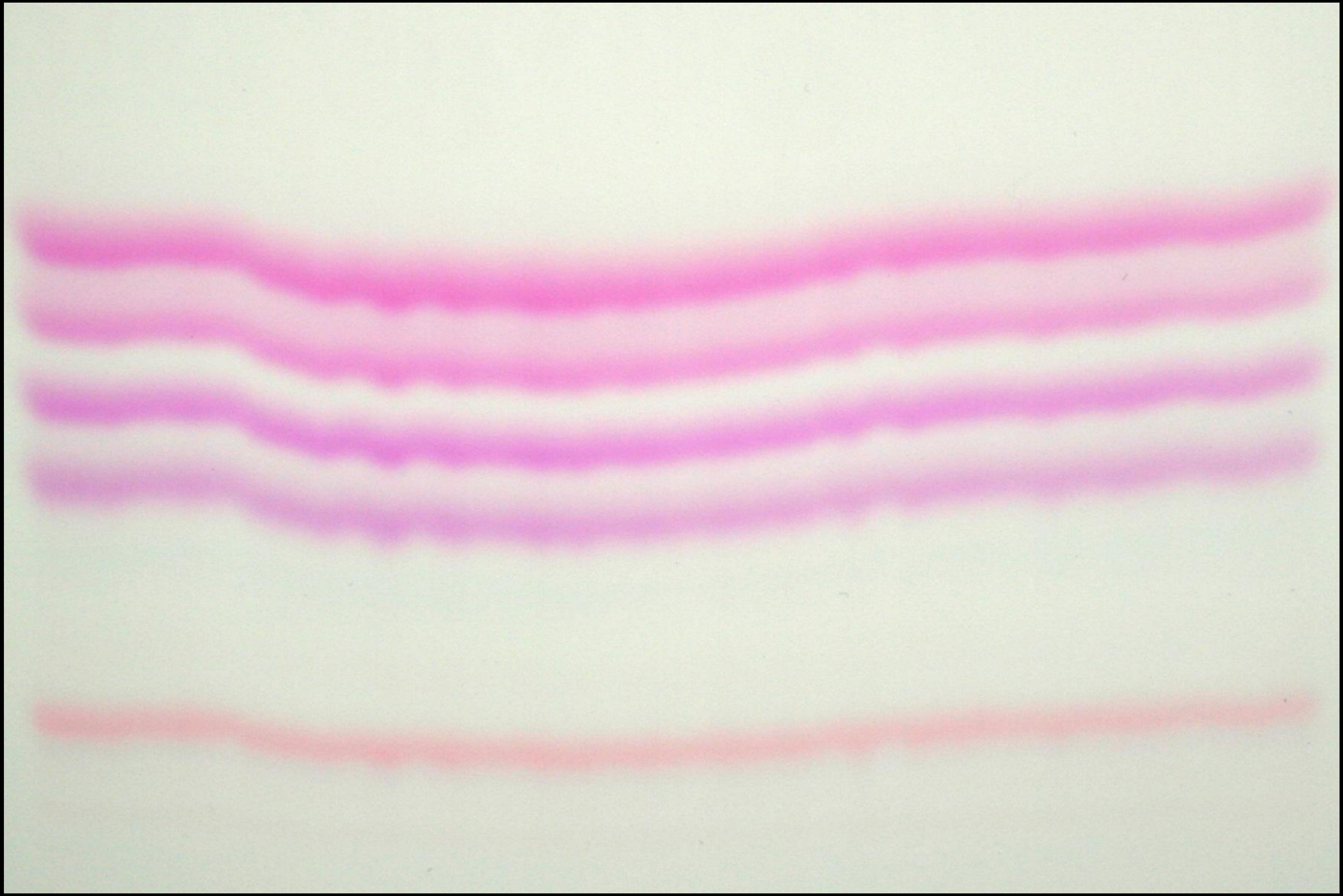


August, 1889
St. Rémy

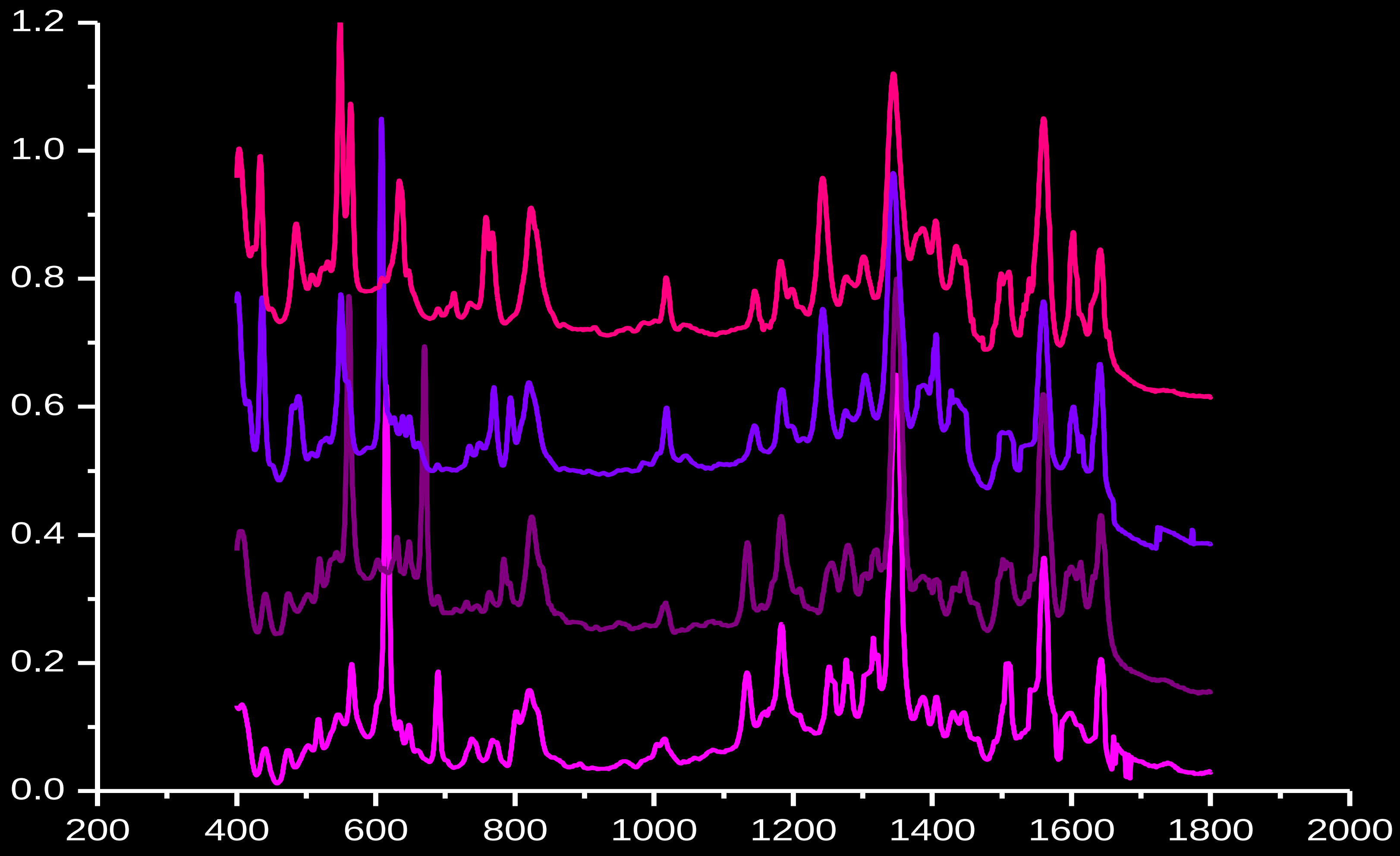
F 626


Raman Intensity
0
5000
10000
15000
20000
500
1000
1500
-40
-20
0
20
40
40
30
20
10
0
-10
-20
-30
-40
Van Gogh sample
eosin reference

TLC-SERS: MAUVEINE



TLC-SERS: MAUVEINE



MAUVEINE IS TOO FLUORESCENT FOR ORDINARY RAMAN AND TOO HIGHLY ABSORBING FOR FT-RAMAN: SERS IS THE ONLY OPTION

SERS ANALYSIS IN PRACTICE

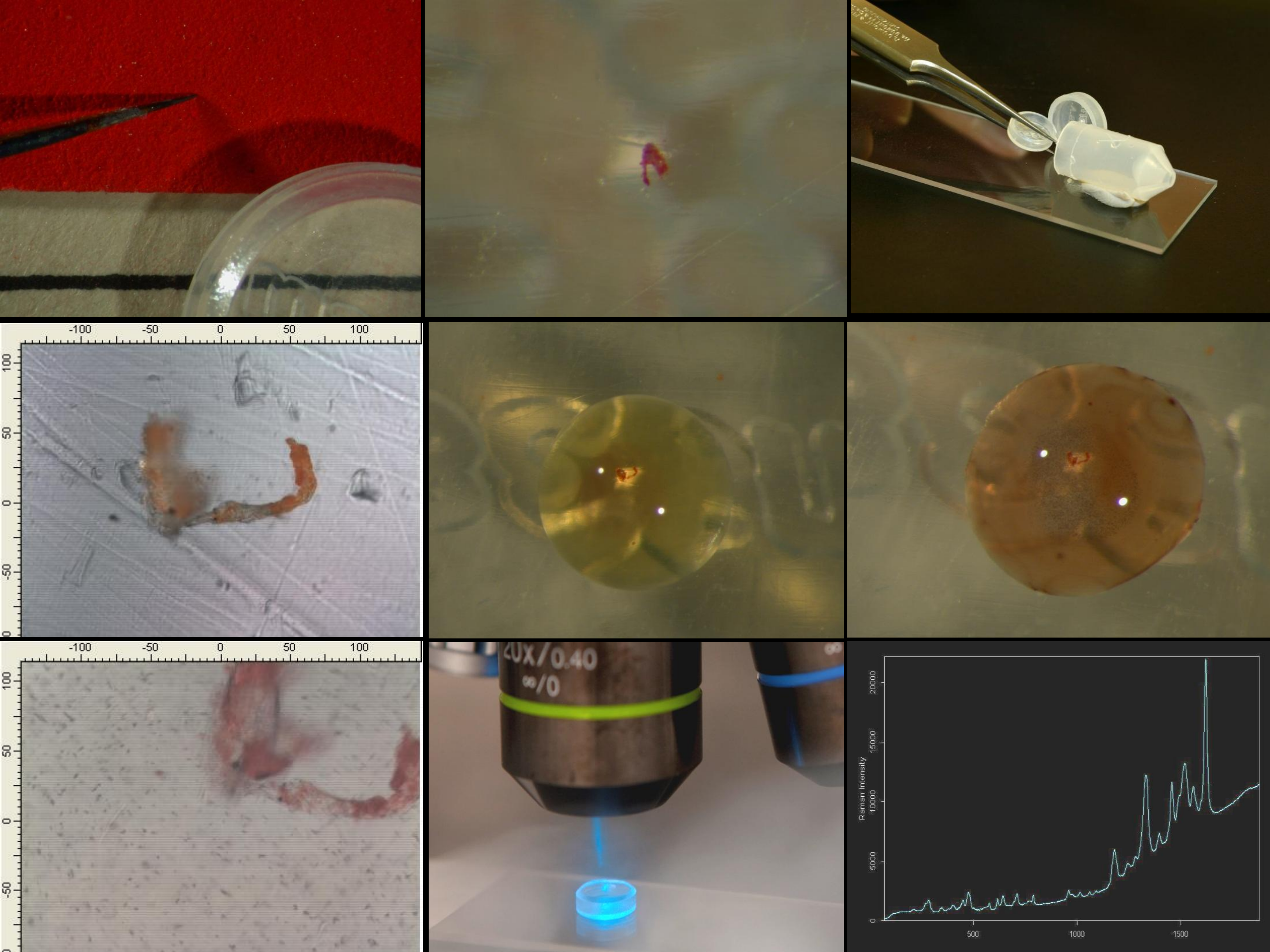
MICROSAMPLING

PRE-TREATMENT OF SAMPLE WITH A “ONE-POT” REACTION TO MAXIMIZE DYE ADSORPTION ON COLLOID AND MINIMIZE LOSSES

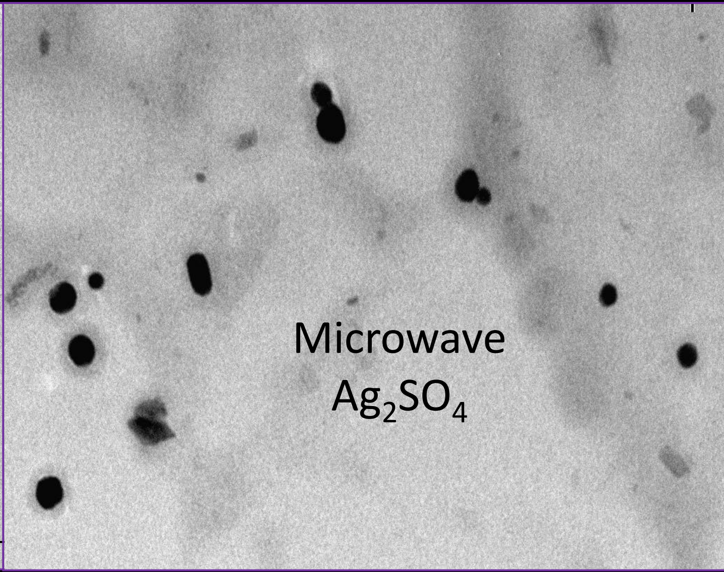
EASILY AND REPRODUCIBLY SYNTHESIZED MONODISPERSE COLLOID: MICROWAVE SUPPORTED GLUCOSE REDUCTION OF SILVER SULFATE IN PRESENCE OF SODIUM CITRATE

RESONANT EXCITATION

SERS SPECTRAL LIBRARY (DYES AND CONTROLLED SUBSTANCES)


-100
-50
0
50
100
20X/0.40
∞/0
Raman Intensity
0
5000
10000
15000
20000
500
1000
1500

COLLOID SYNTHESIS



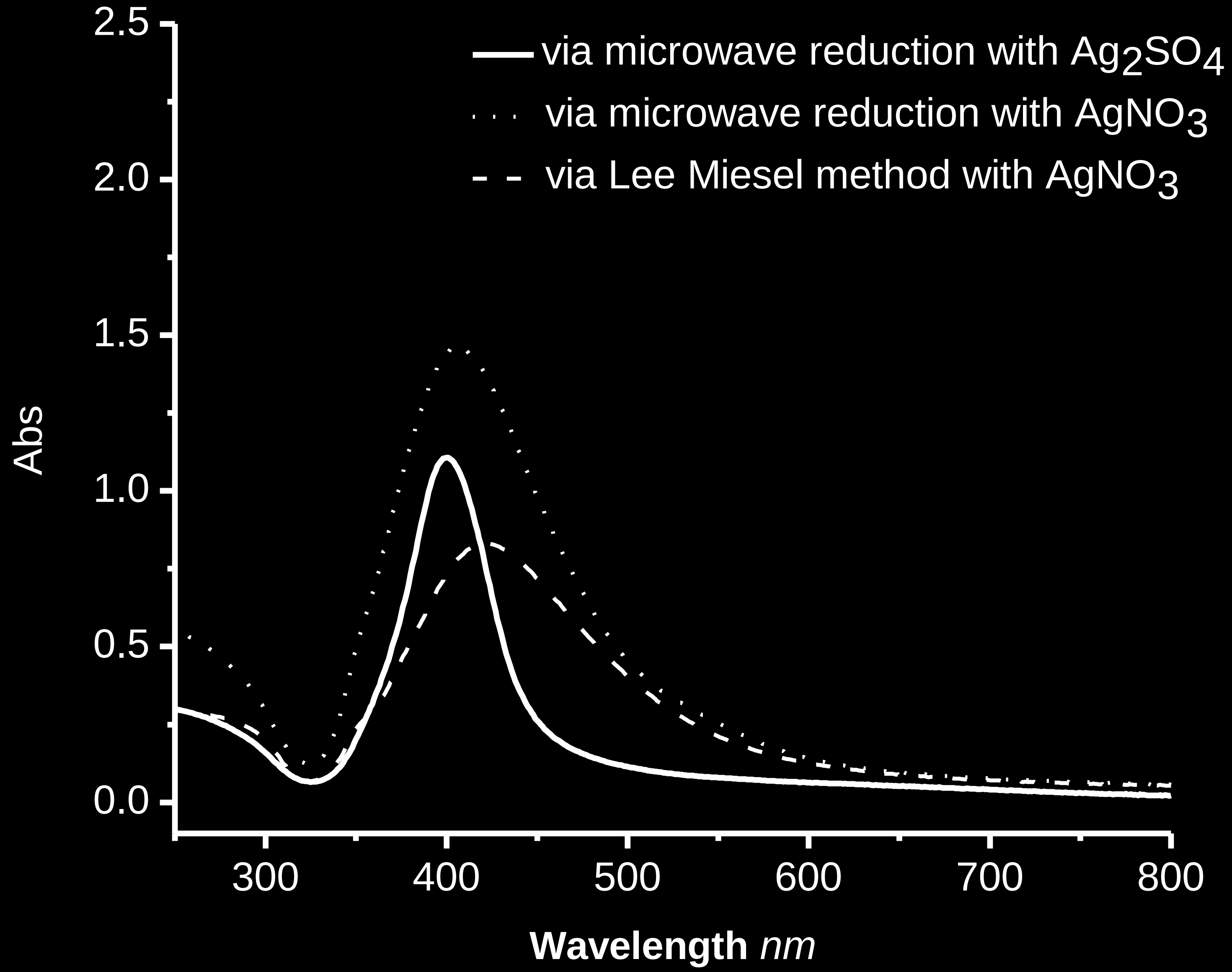
Lee & Meisel Ag NPs ($AgNO_3$ + citrate)

broad absorption (FWHM > 120nm)
broad size distribution (3 - 50 nm)
not stable over time

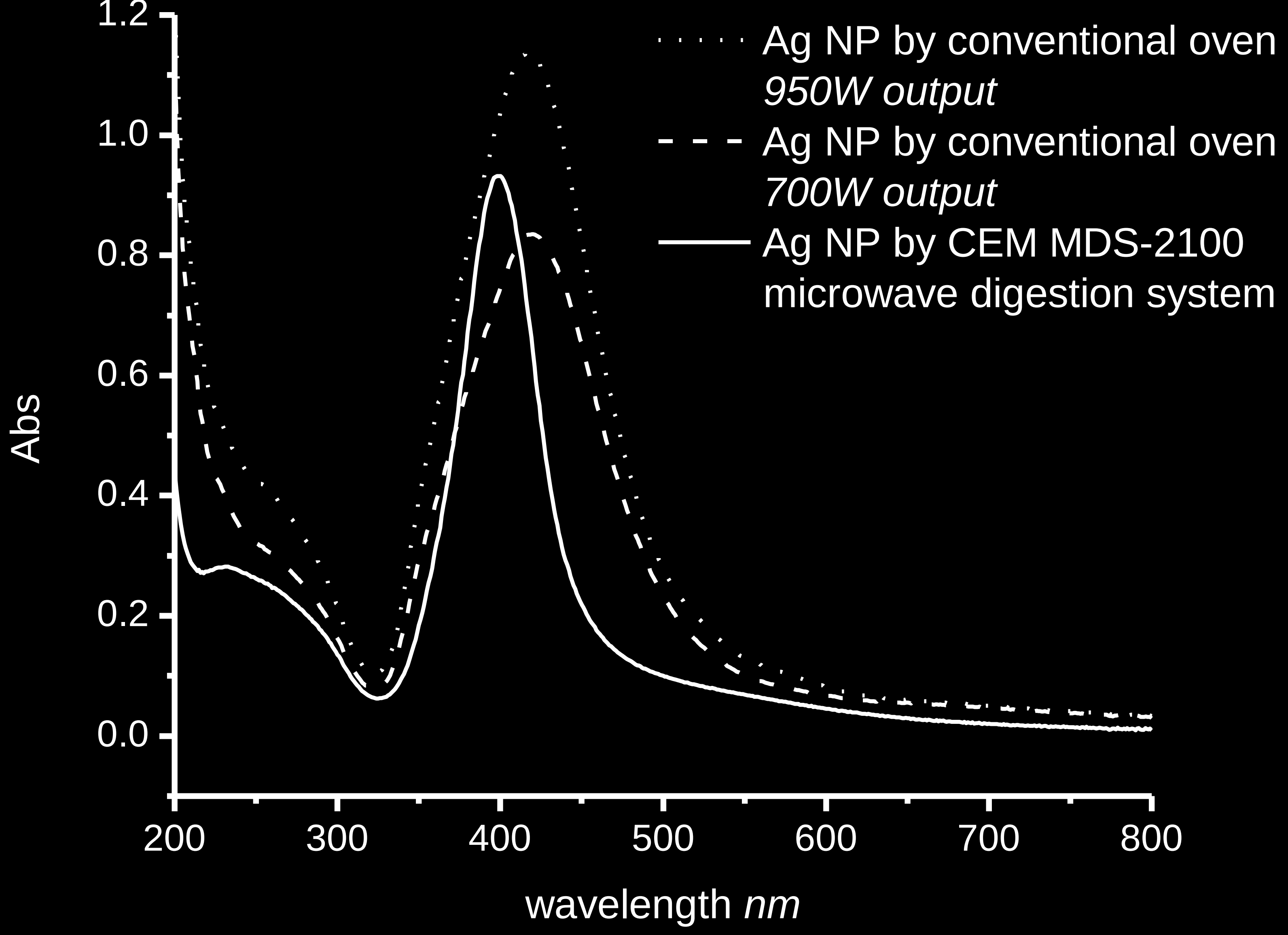
Microwave reduction (Ag_2SO_4 + glucose + citrate)

narrow absorption (FWHM ~ 50 nm)
narrow size distribution (3 - 10 nm)
stable over 5 - 12 months

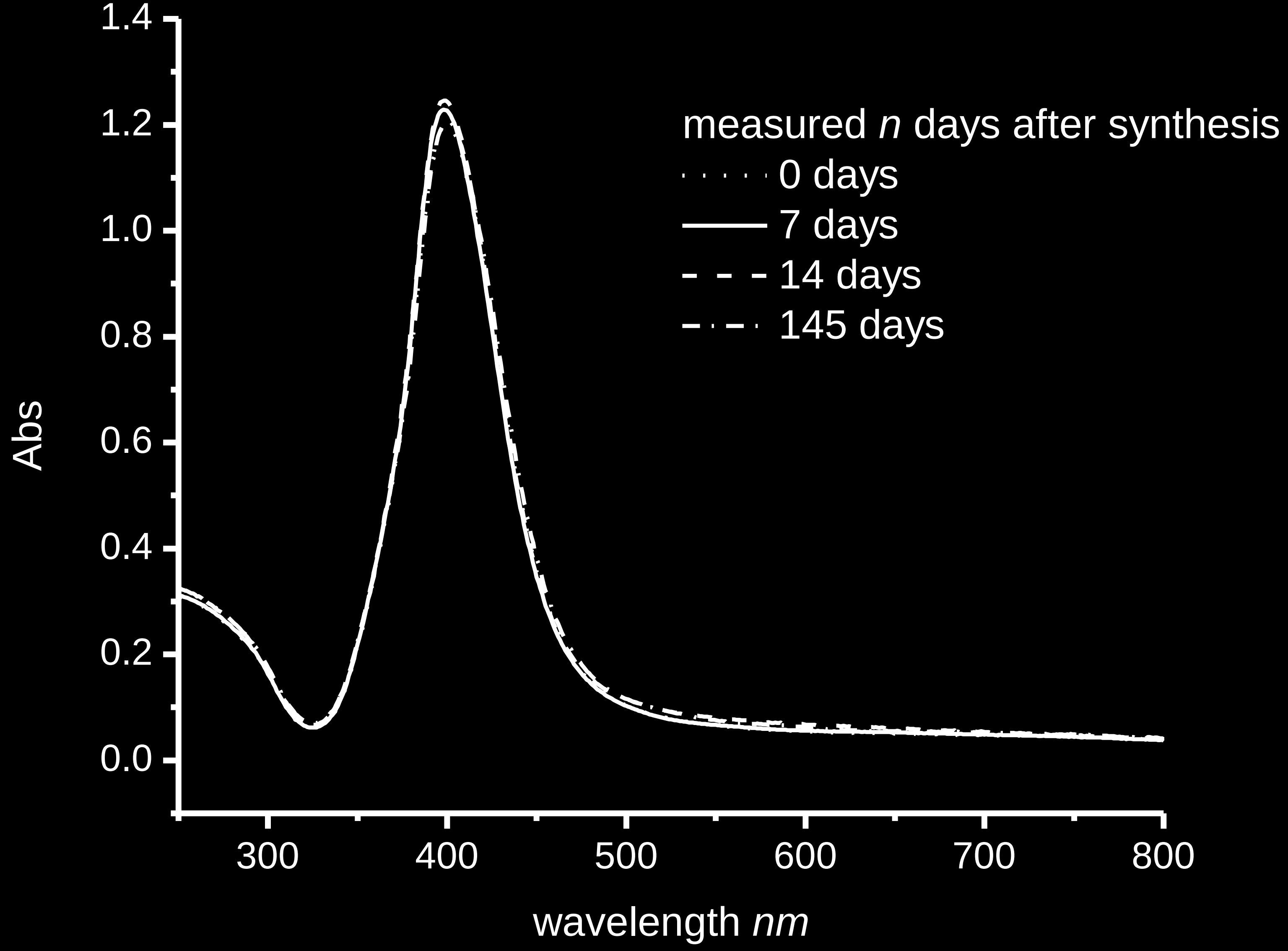
COLLOID SYNTHESIS – METHOD COMPARISON



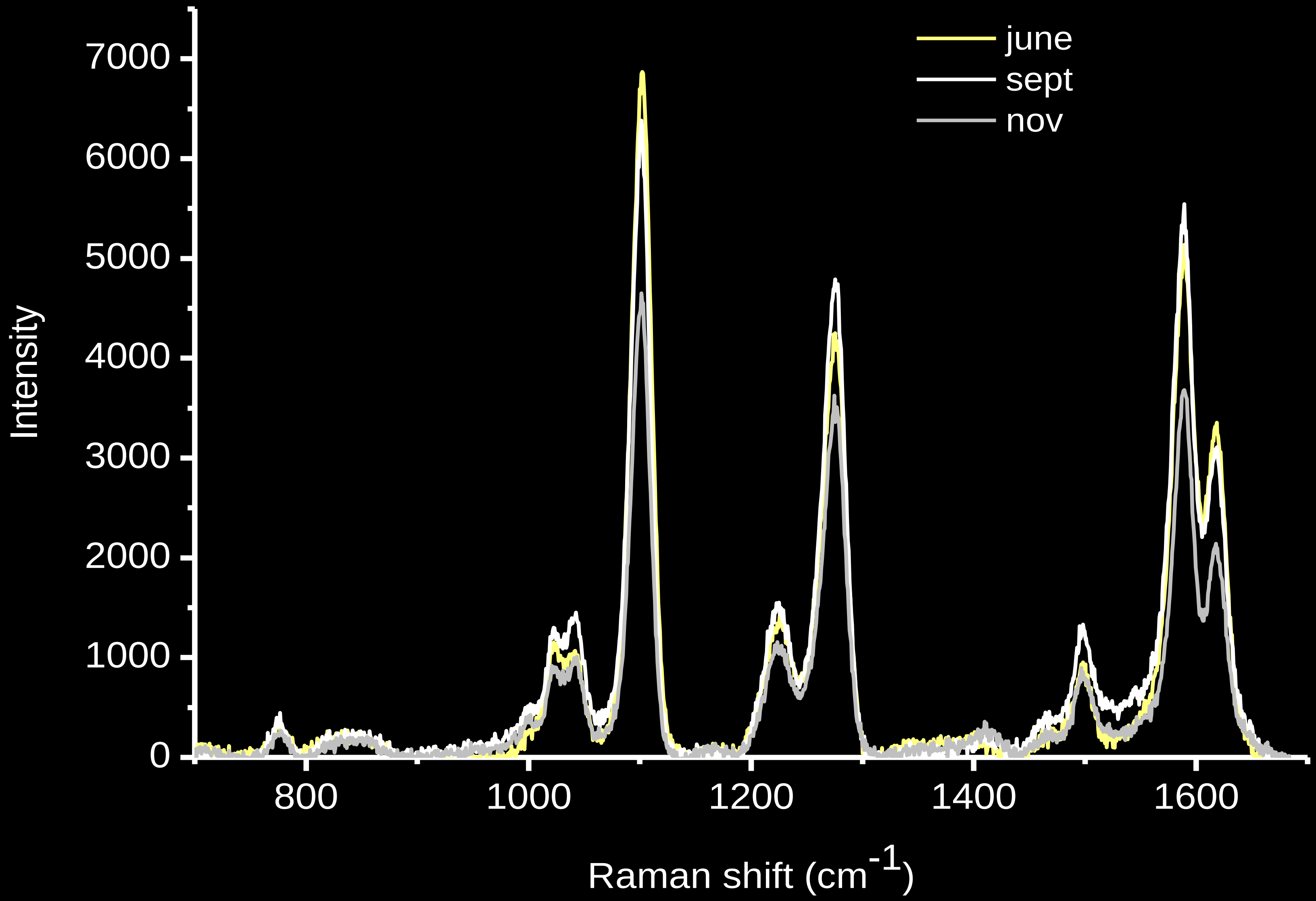
COLLOID SYNTHESIS – MICROWAVE OVEN COMPARISON



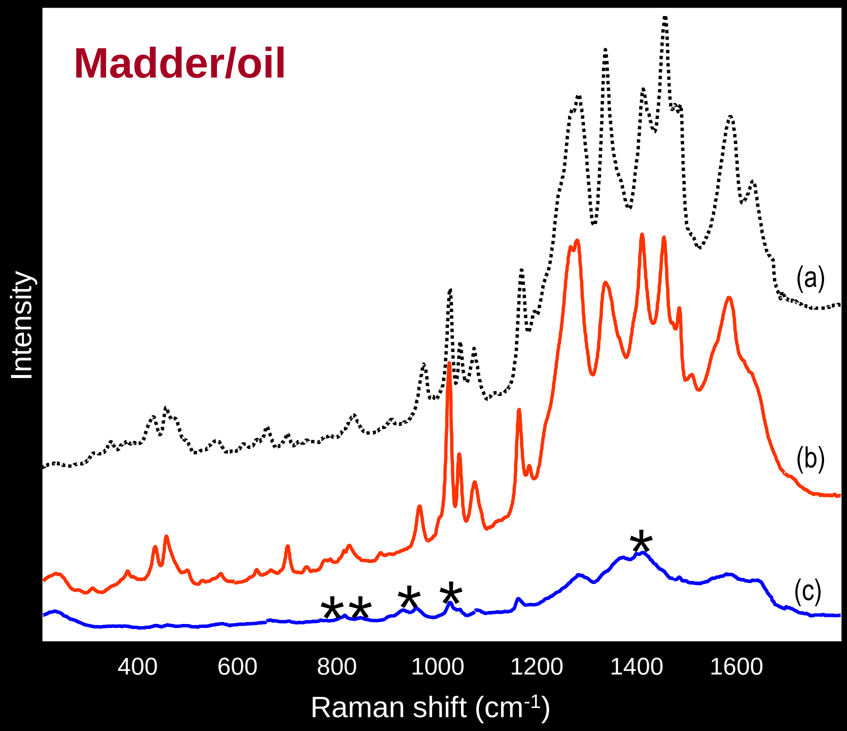
COLLOID STABILITY – OPTICAL ABSORPTION



COLLOID STABILITY - SERS OF 4MPY



SAMPLE TREATMENT



The card players by P. Cézanne
(oil on canvas – 1890-1892)

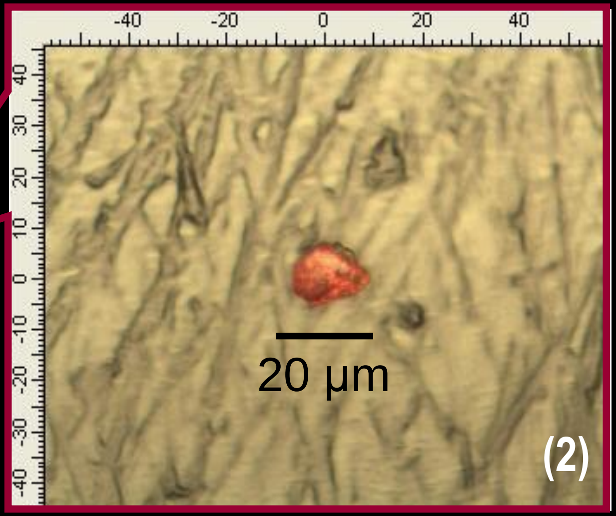
SERS spectra of:

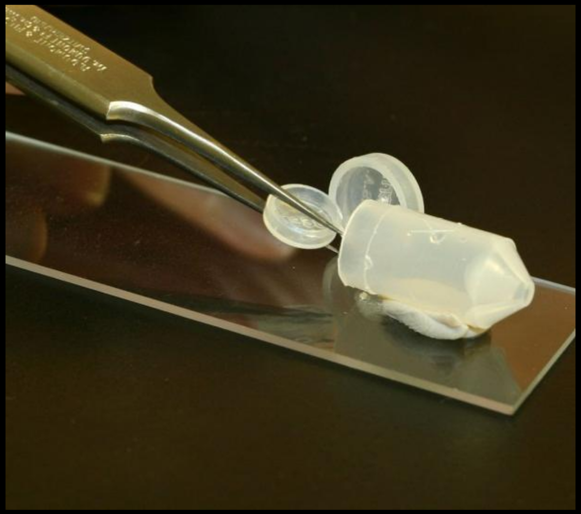
(a) reference madder lake upon HF treatment

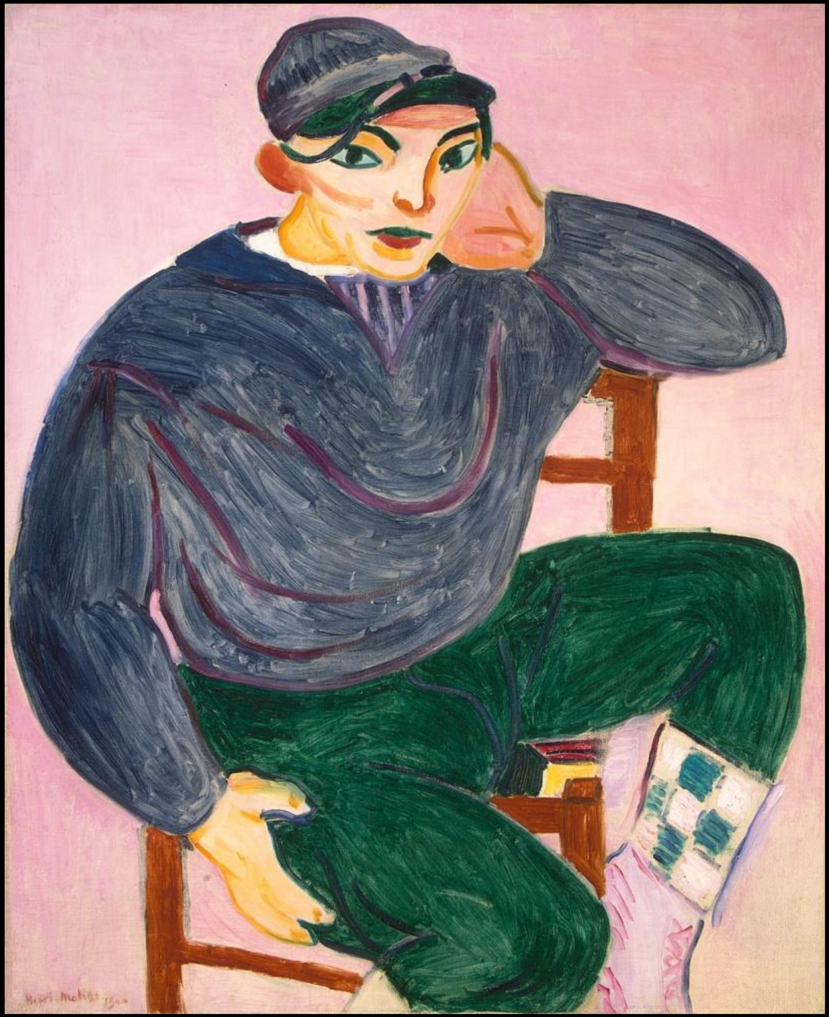
(b) sample on Ag colloid upon HF treatment

(c) sample on 5x Ag colloid without hydrolysis

* Spurious bands due to the colloid

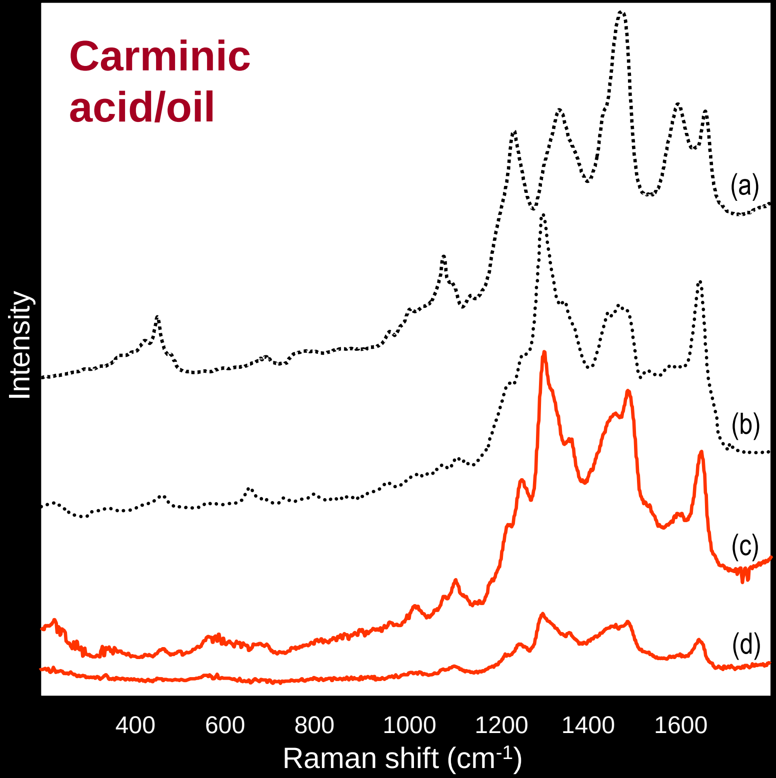






Henri Matisse, *The young sailor*, 1906. Oil on canvas, 40 x 32 3/4 inches (101.6 x 83.2 cm) . The Metropolitan Museum of Art, 1999.363.41. Jacques and Natasha Gelman Collection, 1998.

The young sailor by H. Matisse (oil on canvas – 1906)



SERS spectra of:

(a) reference carminic acid at pH=2

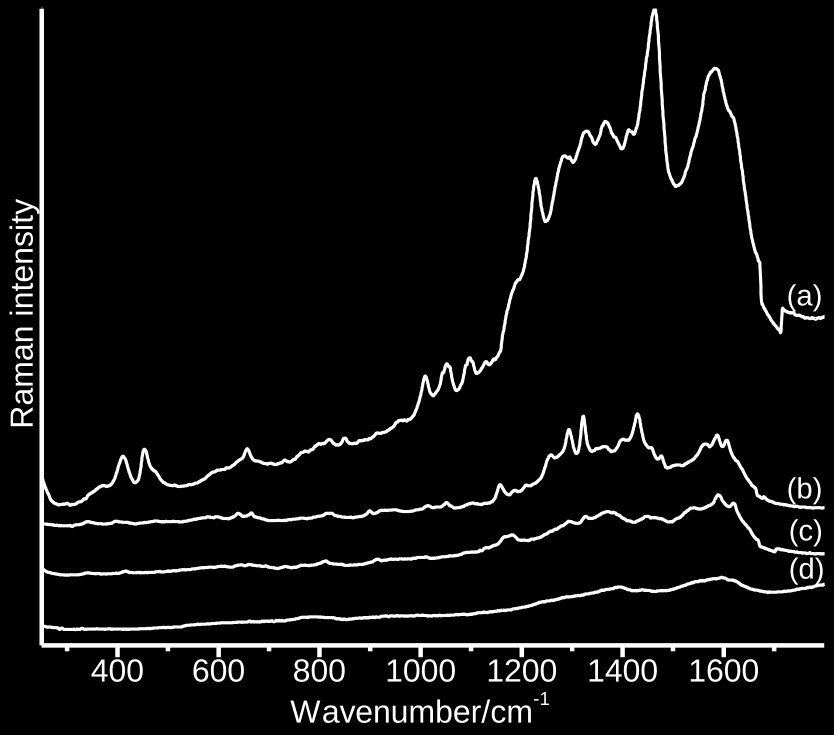
(b) reference carmine lake without hydrolysis

(c) sample on 5x Ag colloid upon HF treatment without KNO_3

(d) sample on 5x Ag colloid upon HF treatment with KNO_3

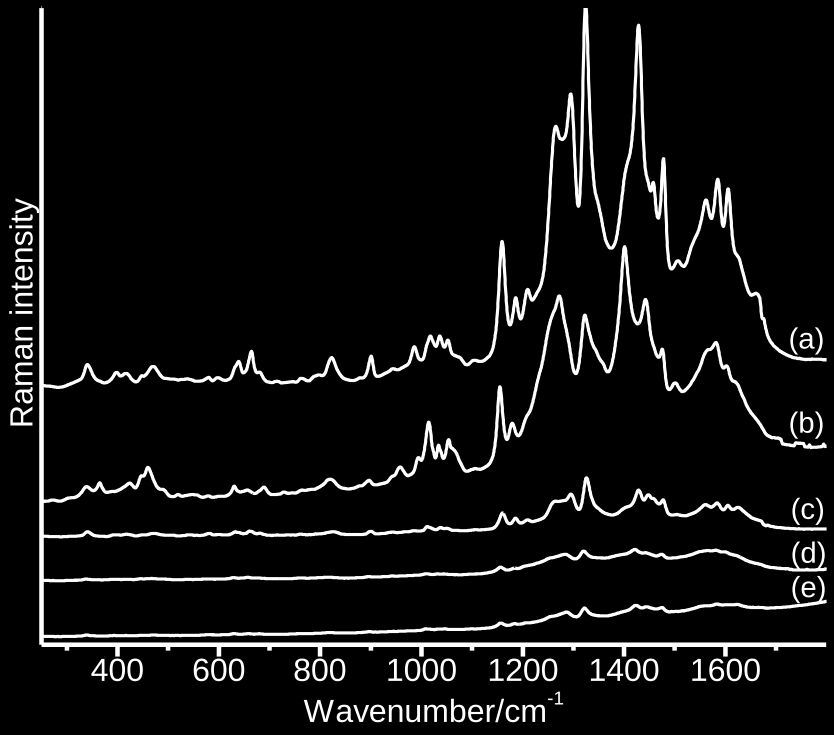
REFERENCE DYED TEXTILES

Lac dye on wool



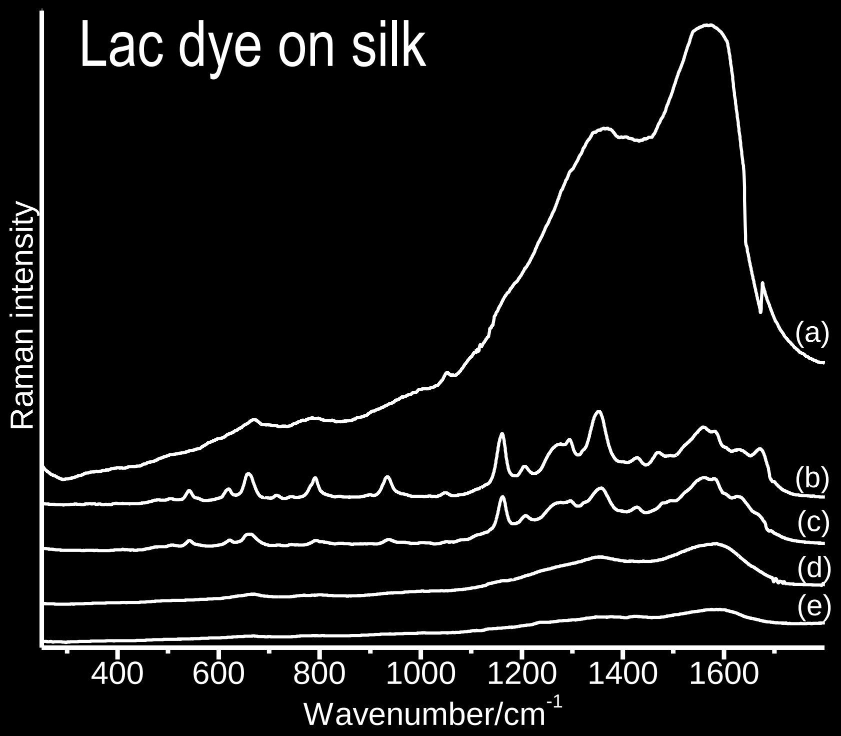
(a) Ag microwave colloid - HF treatment
(b) 5x Ag microwave colloid without HF
(c) Ag microwave colloid without HF
(d) photoreduction of a 10^{-3} M $AgNO_3$ solution

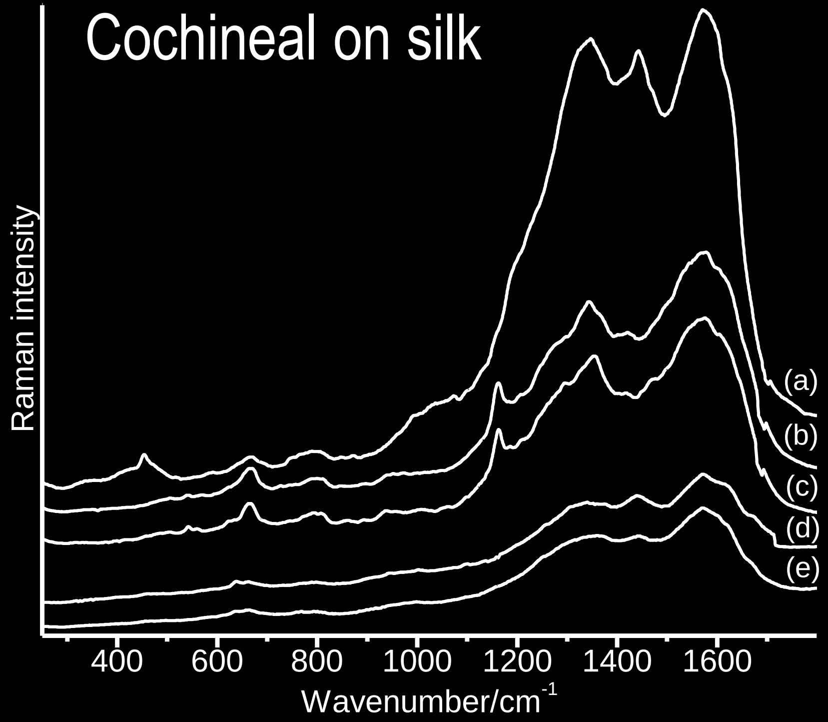
Turkish madder on wool



(a) 5x Ag microwave colloid without extraction,
(b) Ag microwave colloid - HF treatment
(c) Ag microwave colloid without HF
(d) photoreduction of a 10^{-3} M $AgNO_3$ solution
(e) photoreduction of a 10^{-4} M $AgNO_3$ solution.

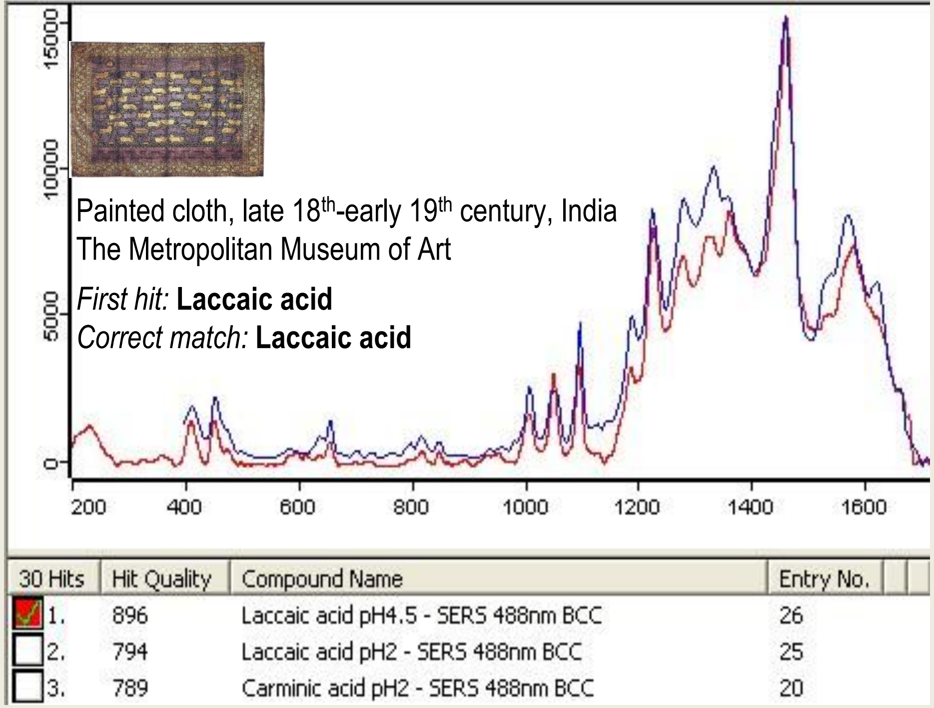
REFERENCE DYED TEXTILES





(a) Ag microwave colloid - HF treatment
(b) 5x Ag microwave colloid without HF
(c) Ag microwave colloid without HF
(d) photoreduction of 10^{-3} M $AgNO_3$
(e) photoreduction of 10^{-4} M $AgNO_3$

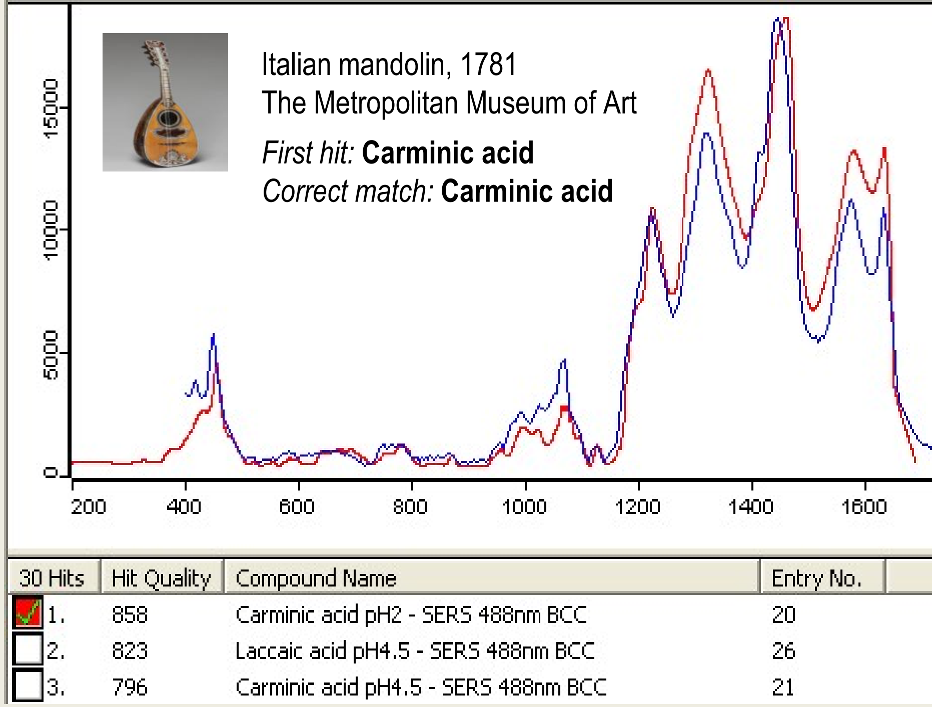
LIBRARY SEARCH AND MATCH



Painted cloth, late 18th-early 19th century, India
The Metropolitan Museum of Art

First hit: **Laccaic acid**
Correct match: **Laccaic acid**

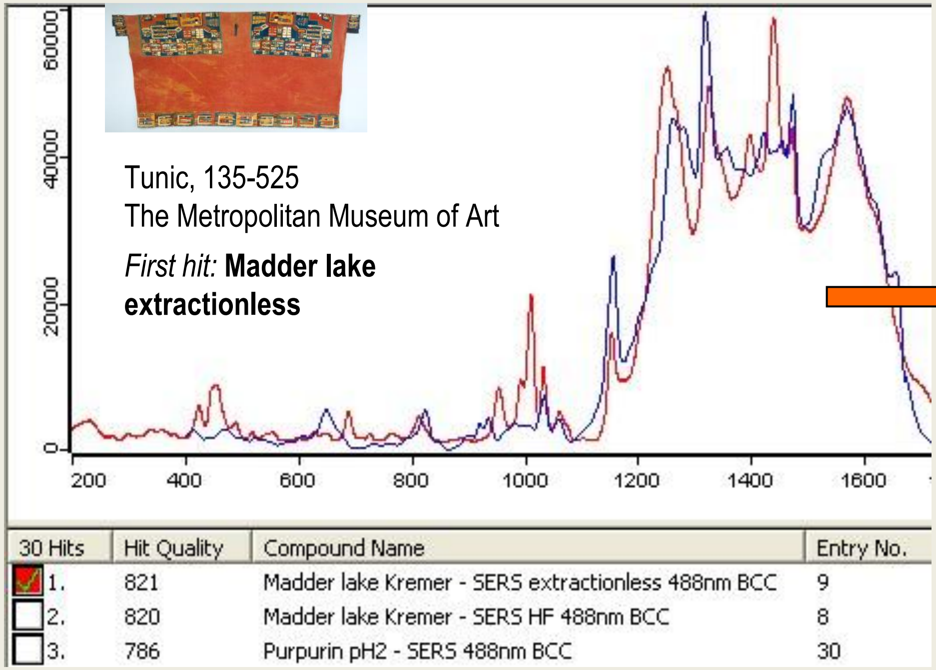
30 Hits	Hit Quality	Compound Name	Entry No.
☑ 1.	896	Laccaic acid pH4.5 - SERS 488nm BCC	26
☐ 2.	794	Laccaic acid pH2 - SERS 488nm BCC	25
☐ 3.	789	Carminic acid pH2 - SERS 488nm BCC	20



Italian mandolin, 1781
The Metropolitan Museum of Art

First hit: **Carminic acid**
Correct match: **Carminic acid**

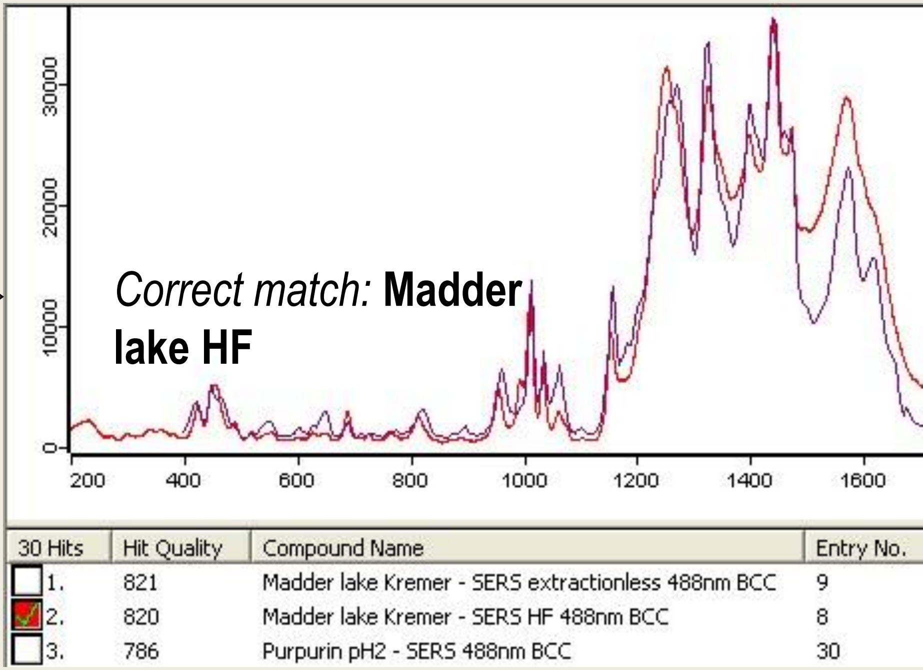
30 Hits	Hit Quality	Compound Name	Entry No.
☑ 1.	858	Carminic acid pH2 - SERS 488nm BCC	20
☐ 2.	823	Laccaic acid pH4.5 - SERS 488nm BCC	26
☐ 3.	796	Carminic acid pH4.5 - SERS 488nm BCC	21



Tunic, 135-525
The Metropolitan Museum of Art

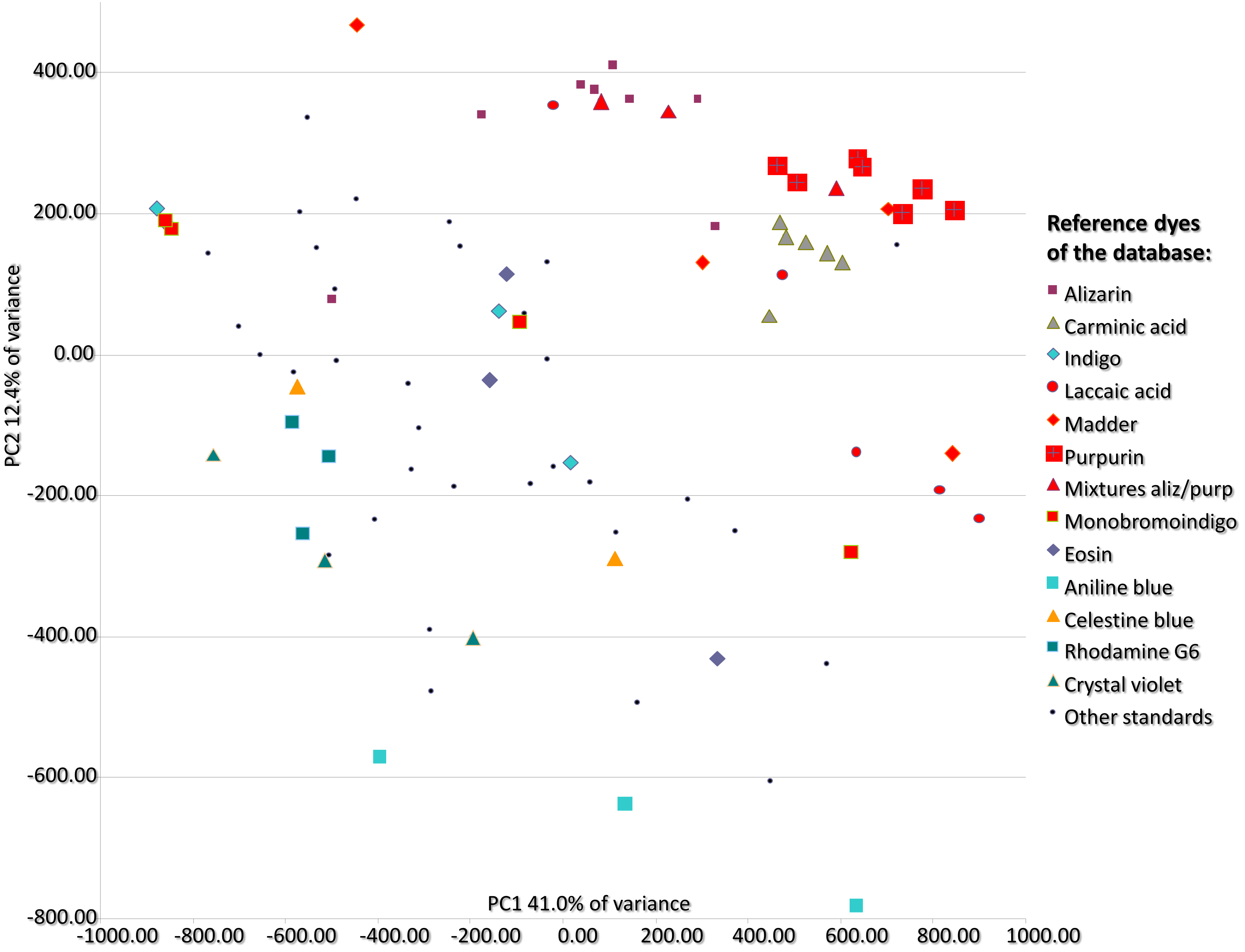
First hit: **Madder lake extractionless**

30 Hits	Hit Quality	Compound Name	Entry No.
☑ 1.	821	Madder lake Kremer - SERS extractionless 488nm BCC	9
☐ 2.	820	Madder lake Kremer - SERS HF 488nm BCC	8
☐ 3.	786	Purpurin pH2 - SERS 488nm BCC	30



Correct match: **Madder lake HF**

30 Hits	Hit Quality	Compound Name	Entry No.
☐ 1.	821	Madder lake Kremer - SERS extractionless 488nm BCC	9
☑ 2.	820	Madder lake Kremer - SERS HF 488nm BCC	8
☐ 3.	786	Purpurin pH2 - SERS 488nm BCC	30


Reference dyes of the database:
Alizarin
Carminic acid
Indigo
Laccaic acid
Madder
Purpurin
Mixtures aliz/purp
Monobromoindigo
Eosin
Aniline blue
Celestine blue
Rhodamine G6
Crystal violet
Other standards
PC2 12.4% of variance
PC1 41.0% of variance
400.00
200.00
0.00
-200.00
-400.00
-600.00
-800.00
-1000.00
-800.00
-600.00
-400.00
-200.00
0.00
200.00
400.00
600.00
800.00
1000.00

NON DESTRUCTIVE SERS?

CROSS-LINKED HYDROXYACRYLATE GEL + SOLVENT/CHELATING AGENT

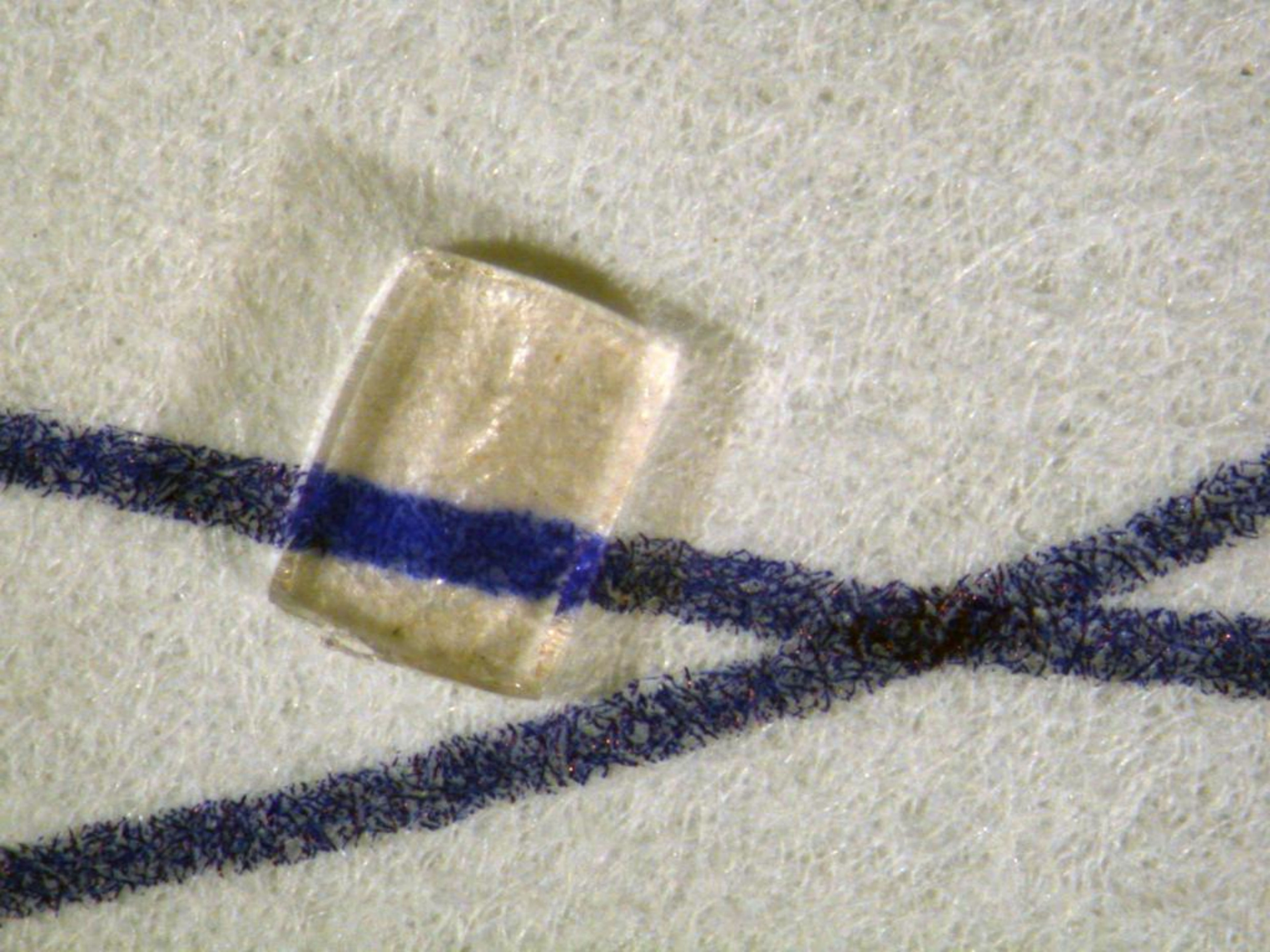
1:1 RANDOM COPOLYMER OF
2,3-DIHYDROXYPROPYL METHACRYLATE WITH 2-HYDROXYETHYL METHACRYLATE

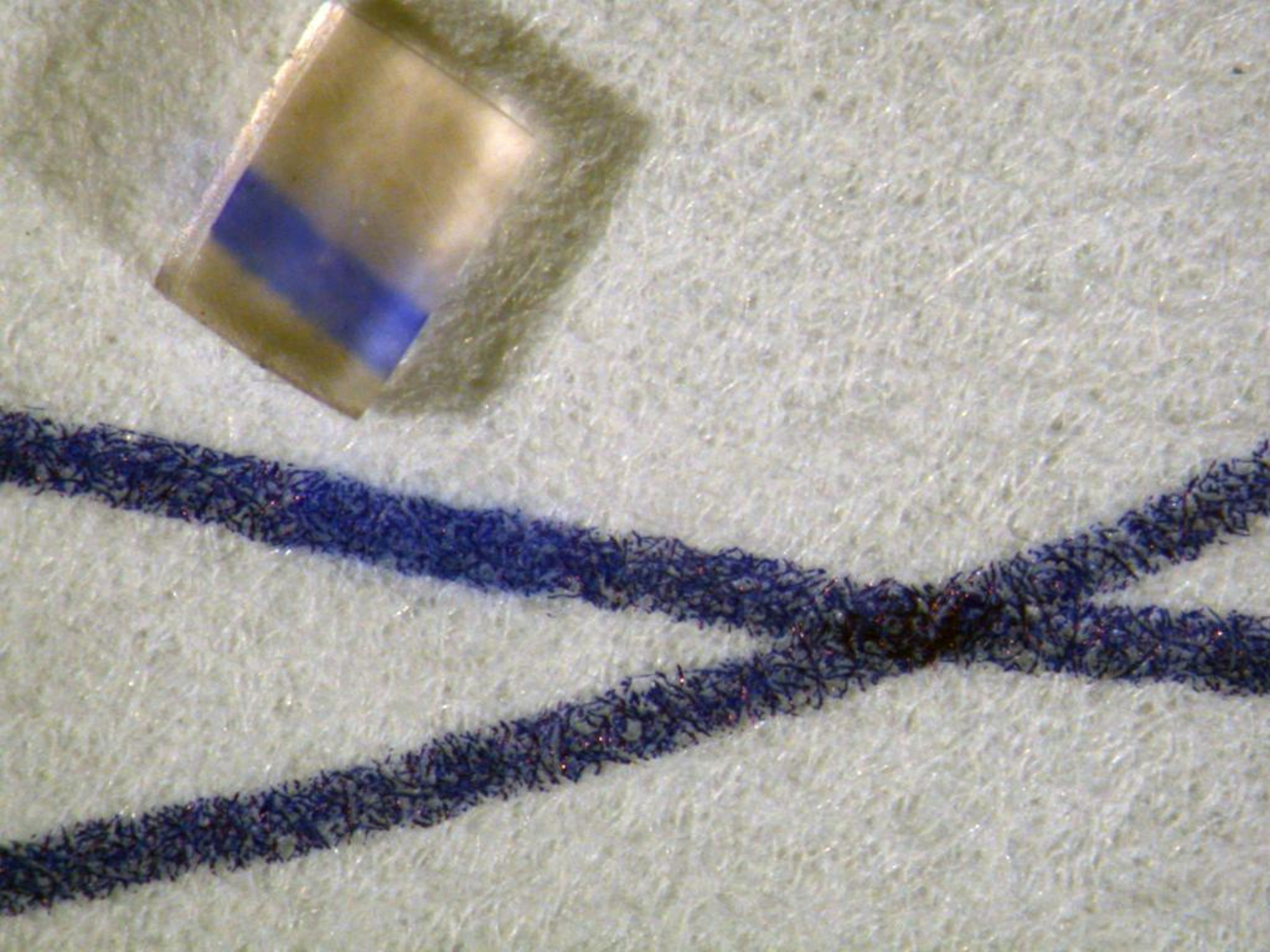
IN SITU HYDROLYSYS/EXTRACTION AND DYE TRANSFER TO GEL

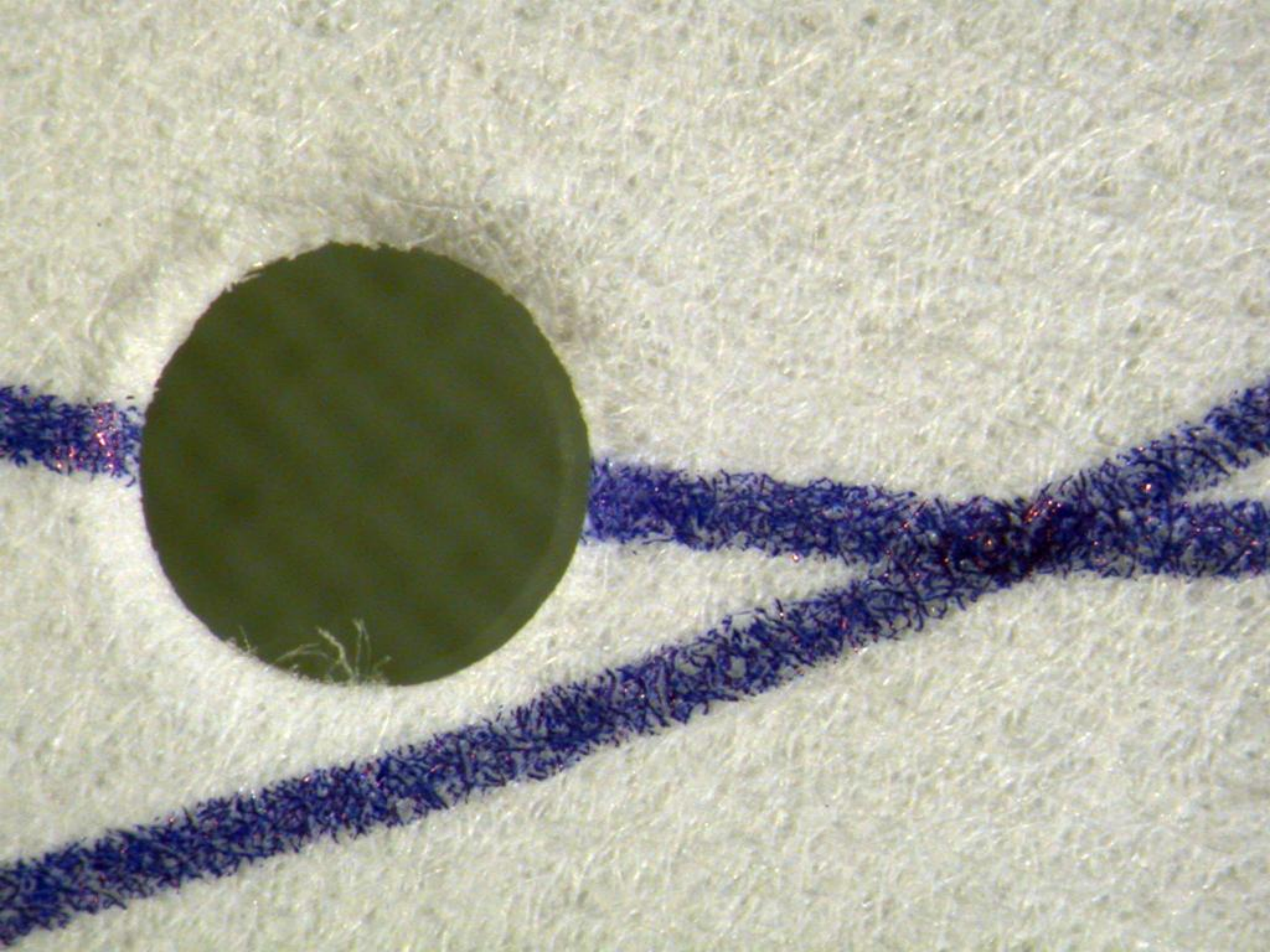
SERS OF GEL

NO MECHANICAL DAMAGE TO SUBSTRATE
NO FADING OF DYE ON SUBSTRATE

Leona M. Non-Invasive identification of fluorescent dyes in historic textiles by matrix-transfer surface-enhanced Raman scattering (MT-SERS). United States Patent and Trademark Office Patent No. 7362431 B2 (4/2008).








浮田中納言
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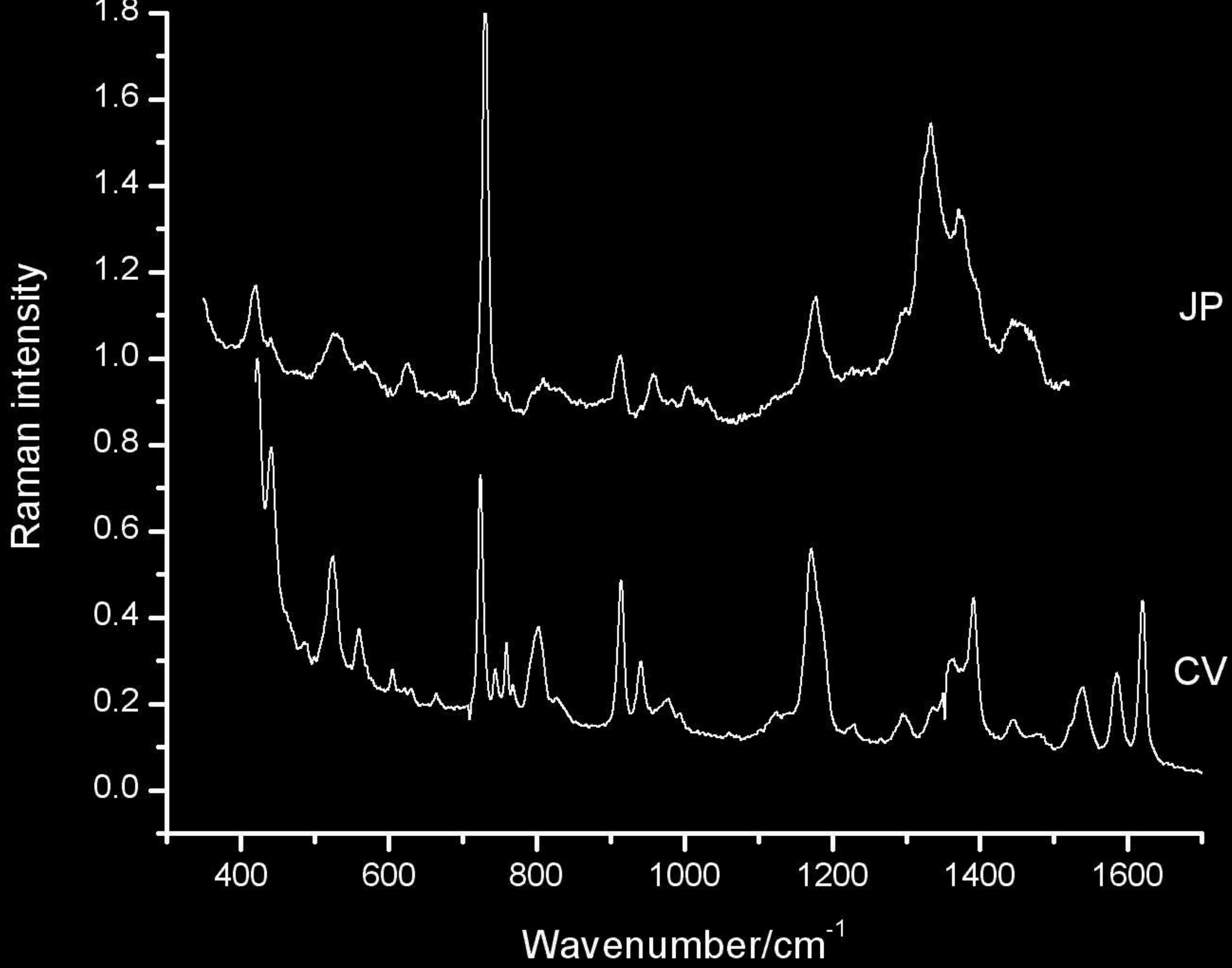
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Raman intensity
400
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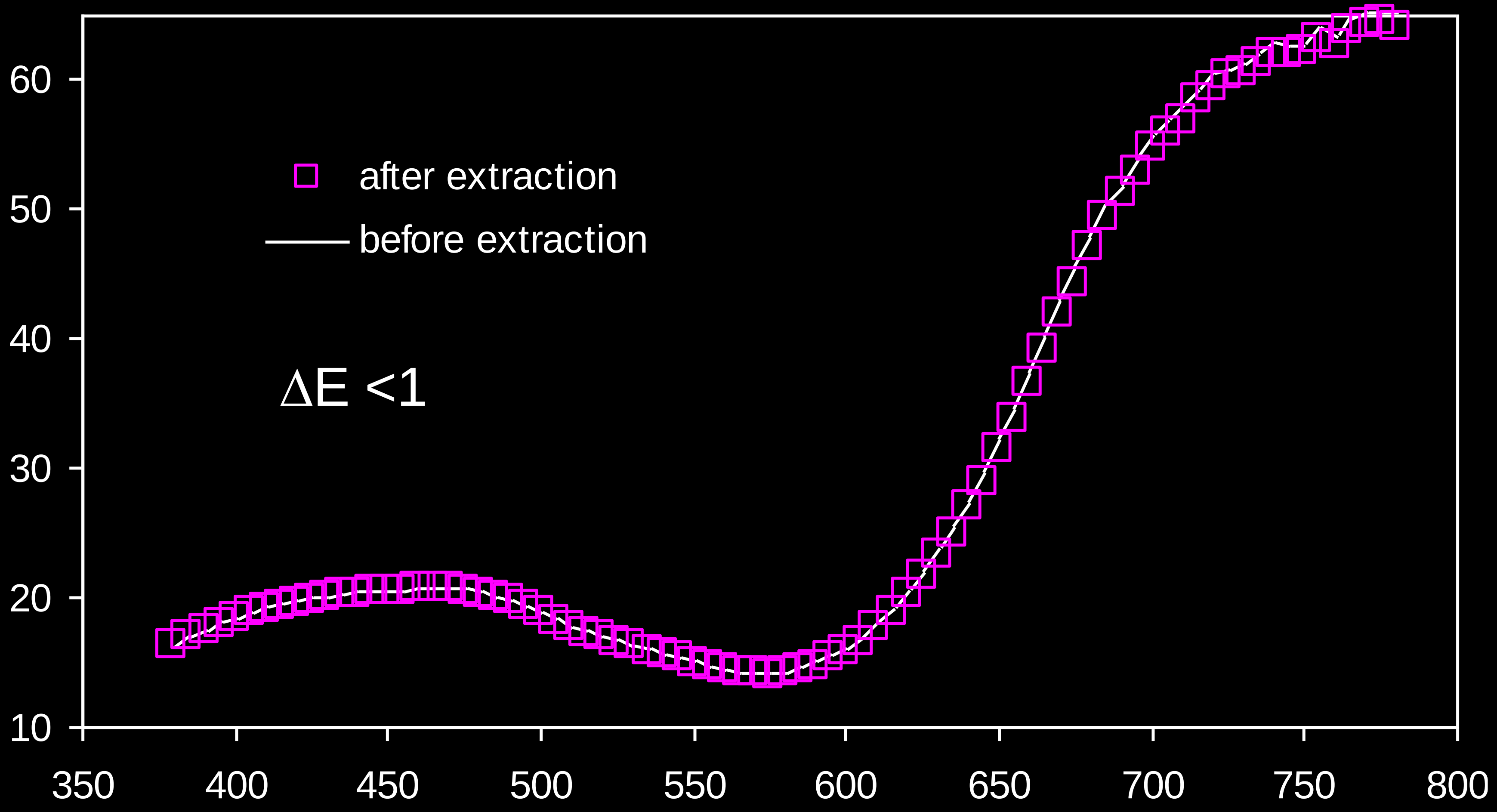
1200
1400
1600
Wavenumber/cm-1
JP
CV

COLOR CHANGE MEASUREMENT BY FIBER OPTICS REFLECTANCE SPECTROSCOPY



10 MEASUREMENTS BEFORE EXTRACTION
SPREAD AROUND MEAN: 0.09 < ΔE < 0.39

10 MEASUREMENTS AFTER EXTRACTION VS PRE-EXTRACTION MEAN:
0.29 < ΔE < 0.67

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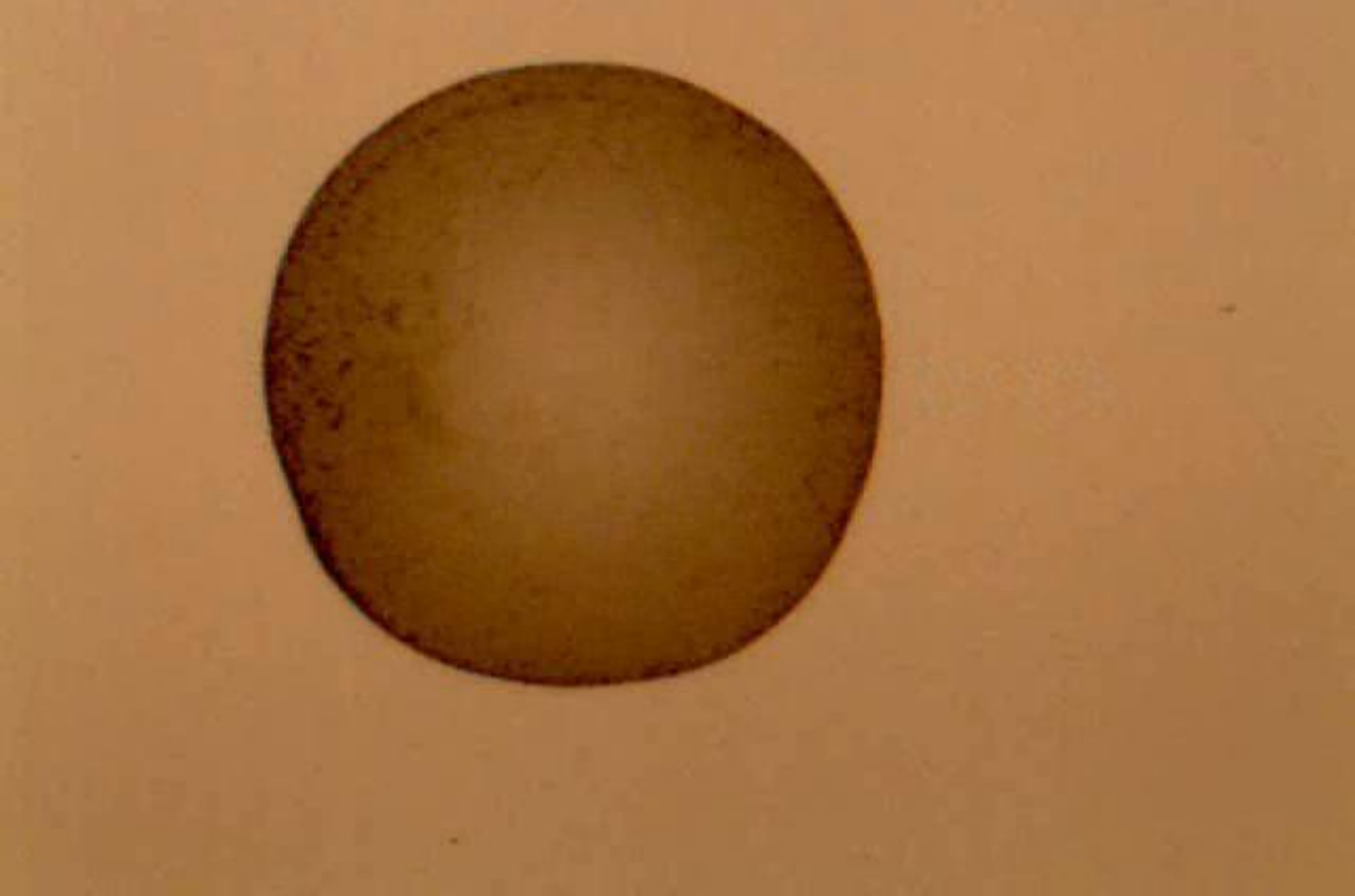

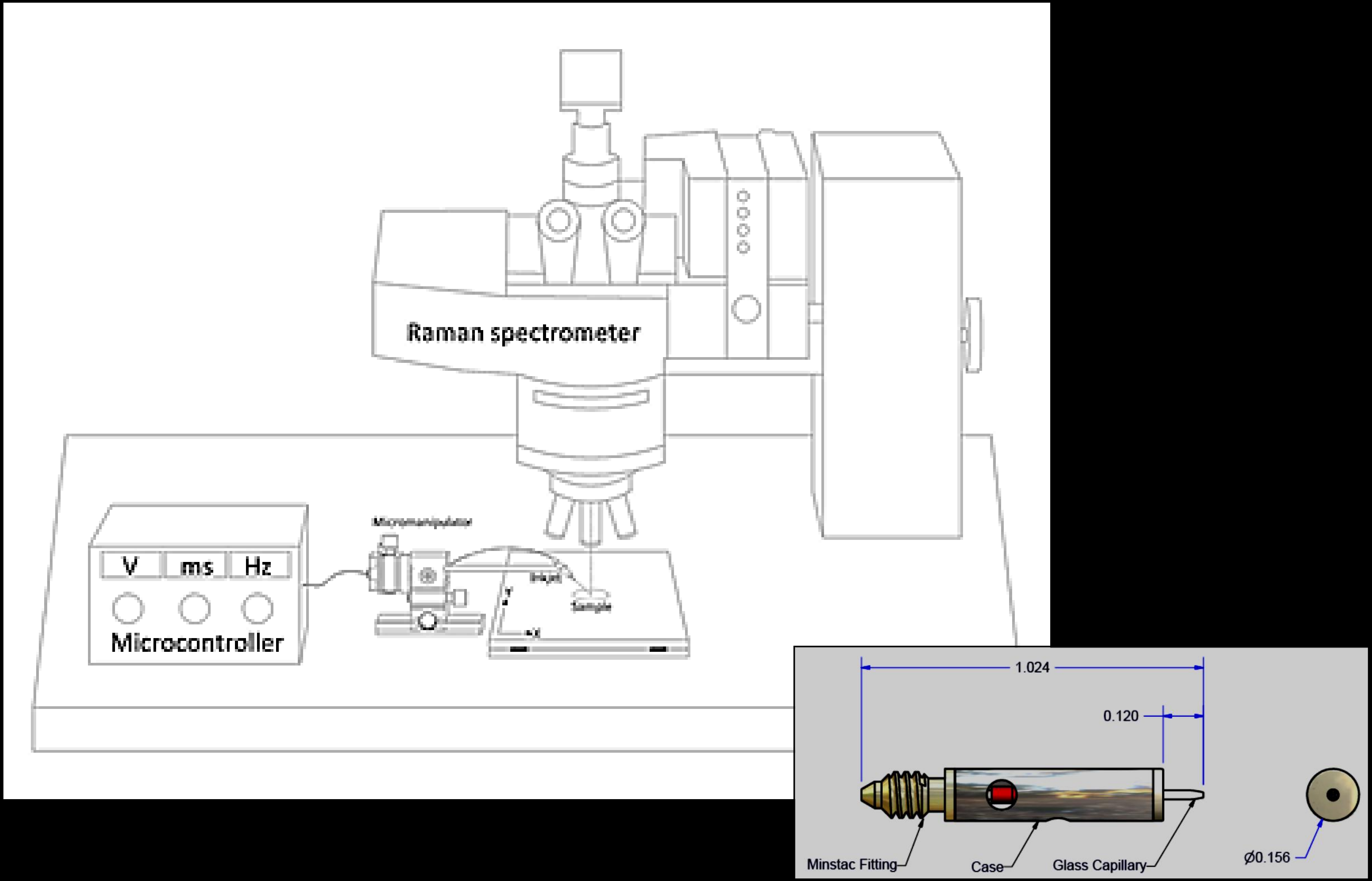

Marco Leona and Thomas J. Tague. Method and Apparatus for in situ Measurement of Materials Properties by Surface Enhanced Raman Spectroscopy. United States Patent and Trademark Office; US 7,787,117 B1. Filed June 24, 2008; awarded August 31, 2010.


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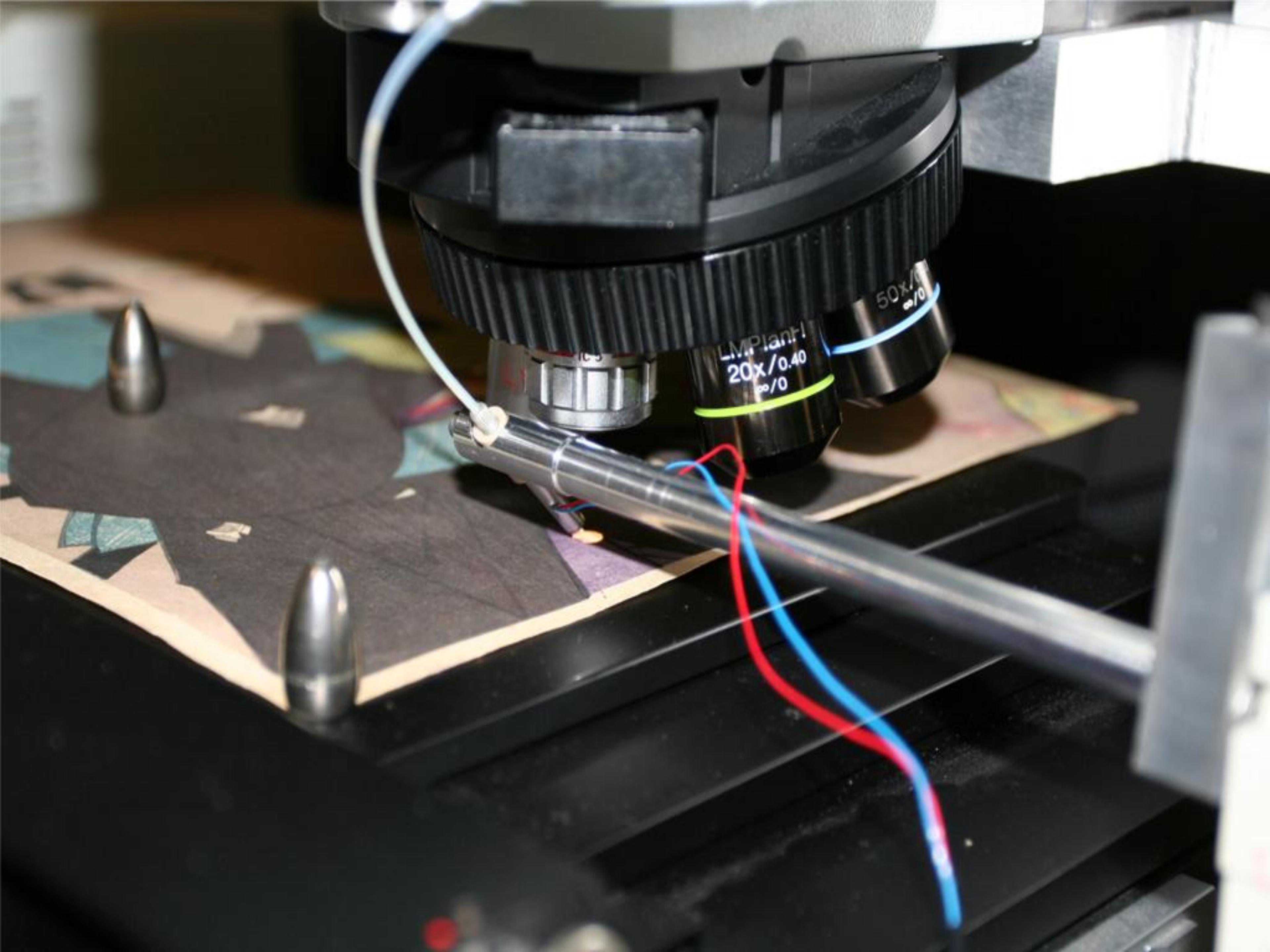
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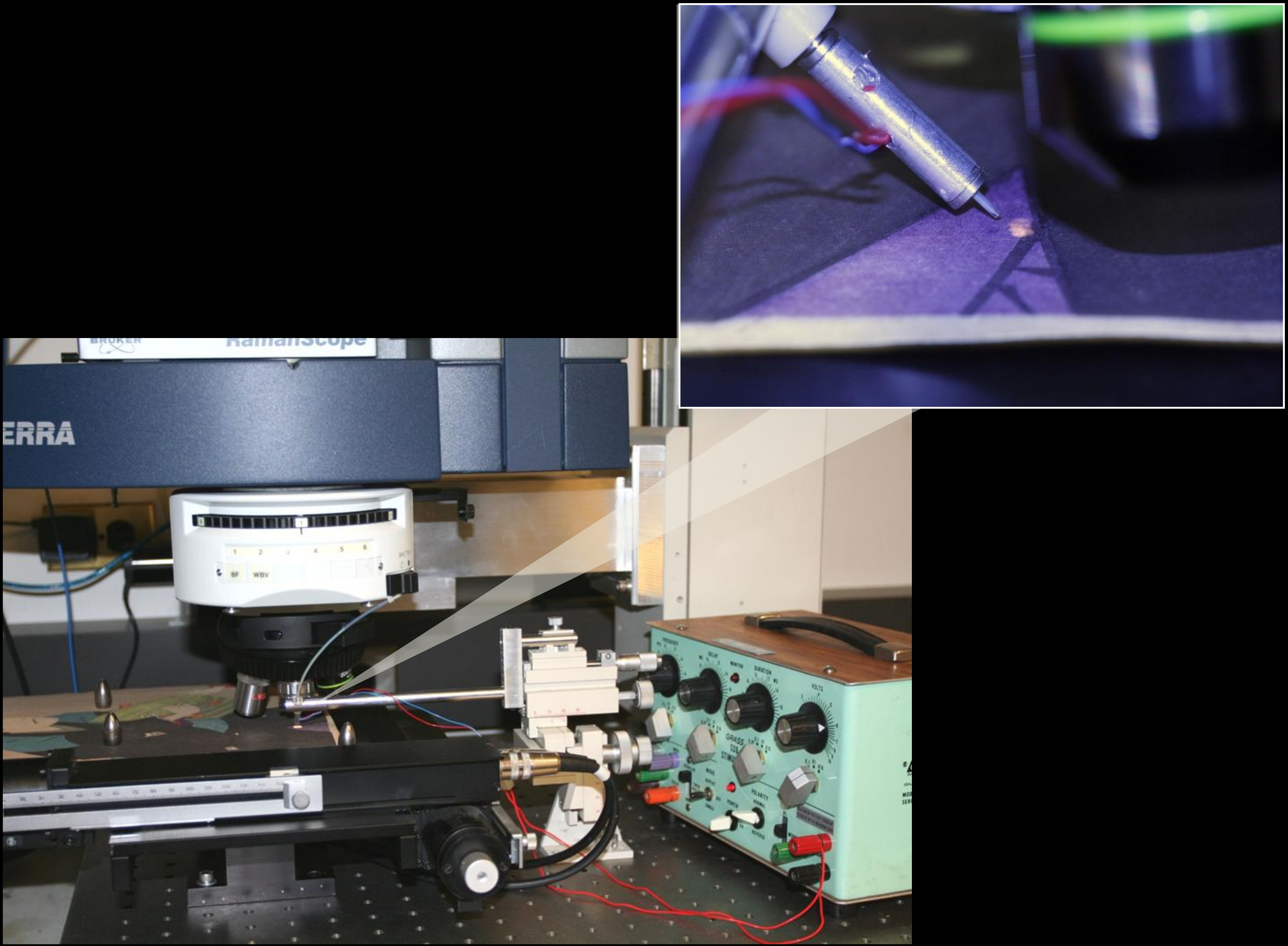
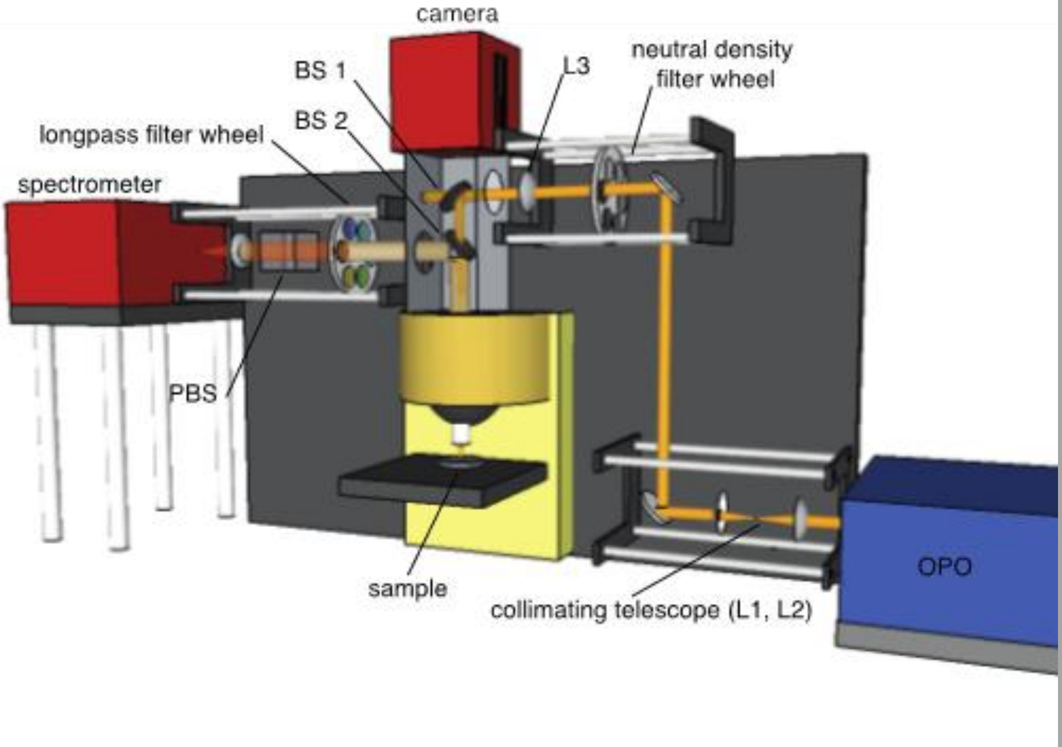
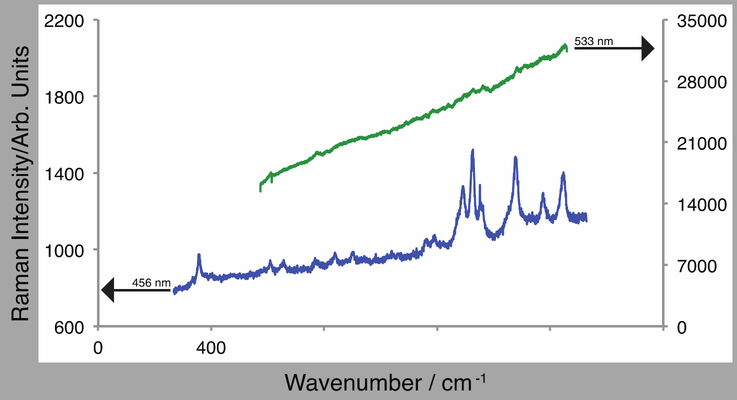
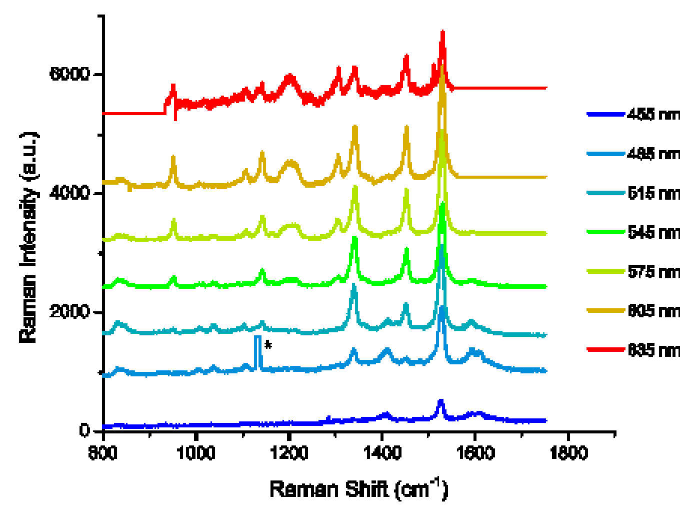
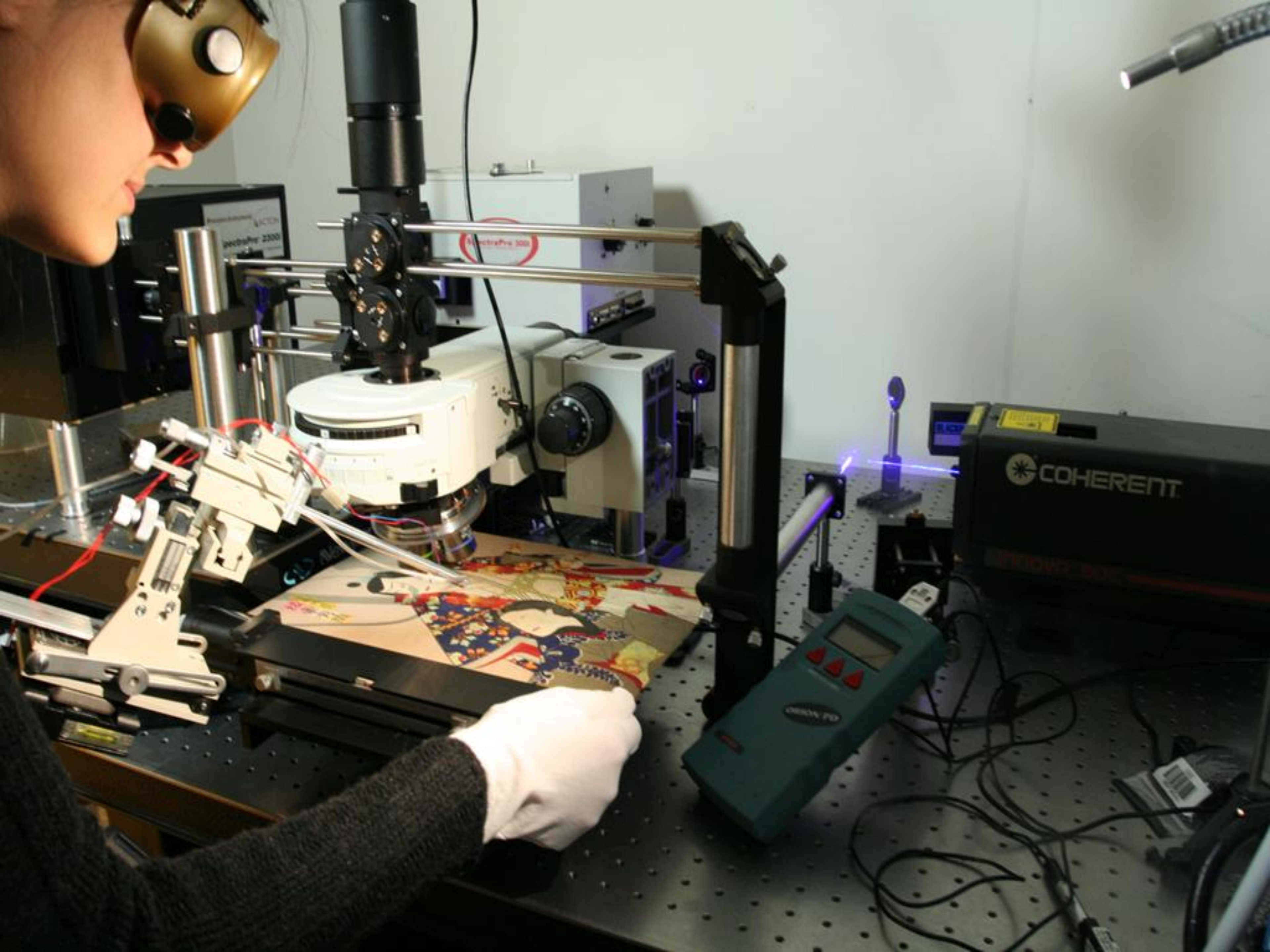

BRUKER
RamanScope
ERRA
BF
WBV
GRASS
VOLTS
DURATION
DELAY
MONITOR
POWER
POLARITY
NORMAL
REVERSE

A COMPACT OPO RAMAN MICROSCOPE FOR WAVELENGTH-TUNABLE MULTI-ANALYTIC MICROANALYSIS





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ACKNOWLEDGEMENTS

John Lombardi, Pablo Londero, Federica Pozzi, Deanna o'Donnell, MariaVega Canamares, Charlie Corredor, Tatyana Teslova, Catherine Chenal, Marques Rich, and Cassidy Alexandre, MMA/CCNY

Thom Kubic, Michelle Miranda, Peter De Cuzzi, Irina Geiman and Vinesh Rana, CUNY-John Jay

Patrick Buzzini and Danielle Kirby, University of West Virginia

Elena Platania, Universita' di Firenze, Italy

Alessa Gambardella, Northwestern University

David Reagan, Southern Connecticut State University

Elena Ferloni, CUNY-QC

Jens Stenger, Harvard University Art Museum

DOJ-NIJ

NSF

The Andrew W. Mellon Foundation

The Camille and Henry Dreyfus Foundation

The David H. Koch Foundation

The Metropolitan Museum of Art

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Synthetic polymers: spectral interpretation

Bruce Chase

University of Delaware, Newark, DE, US; retired DuPont

FRIDAY, SEPTEMBER 28: LECTURE 4

Vibrational Spectroscopy of Polymers
STRUCTURAL AND PHYSICAL EFFECTS

Bruce Chase

IRUG Raman Spectroscopy Workshop

Philadelphia Museum of Art

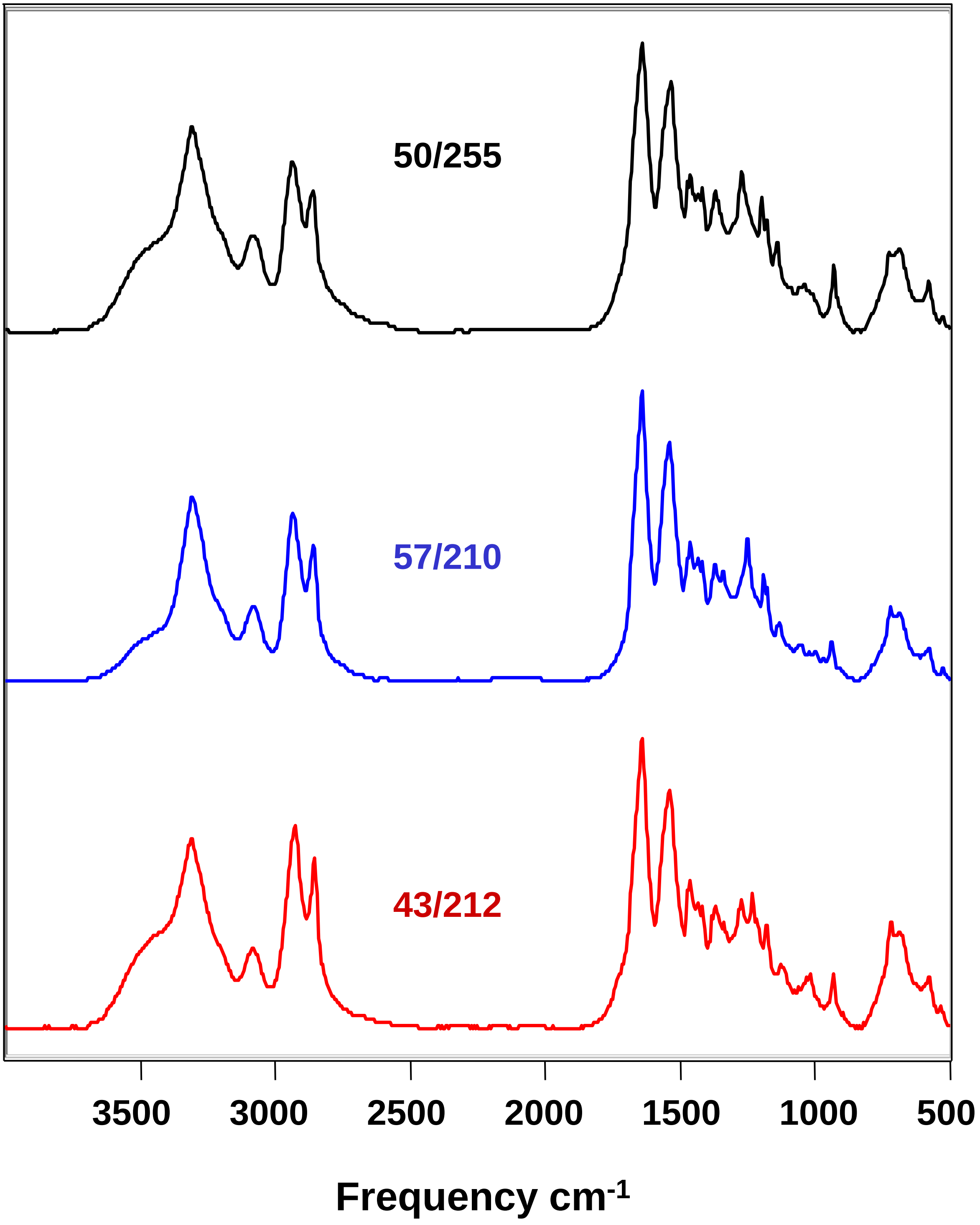
September 28, 2012

Vibrational Spectroscopy in Polymer Science

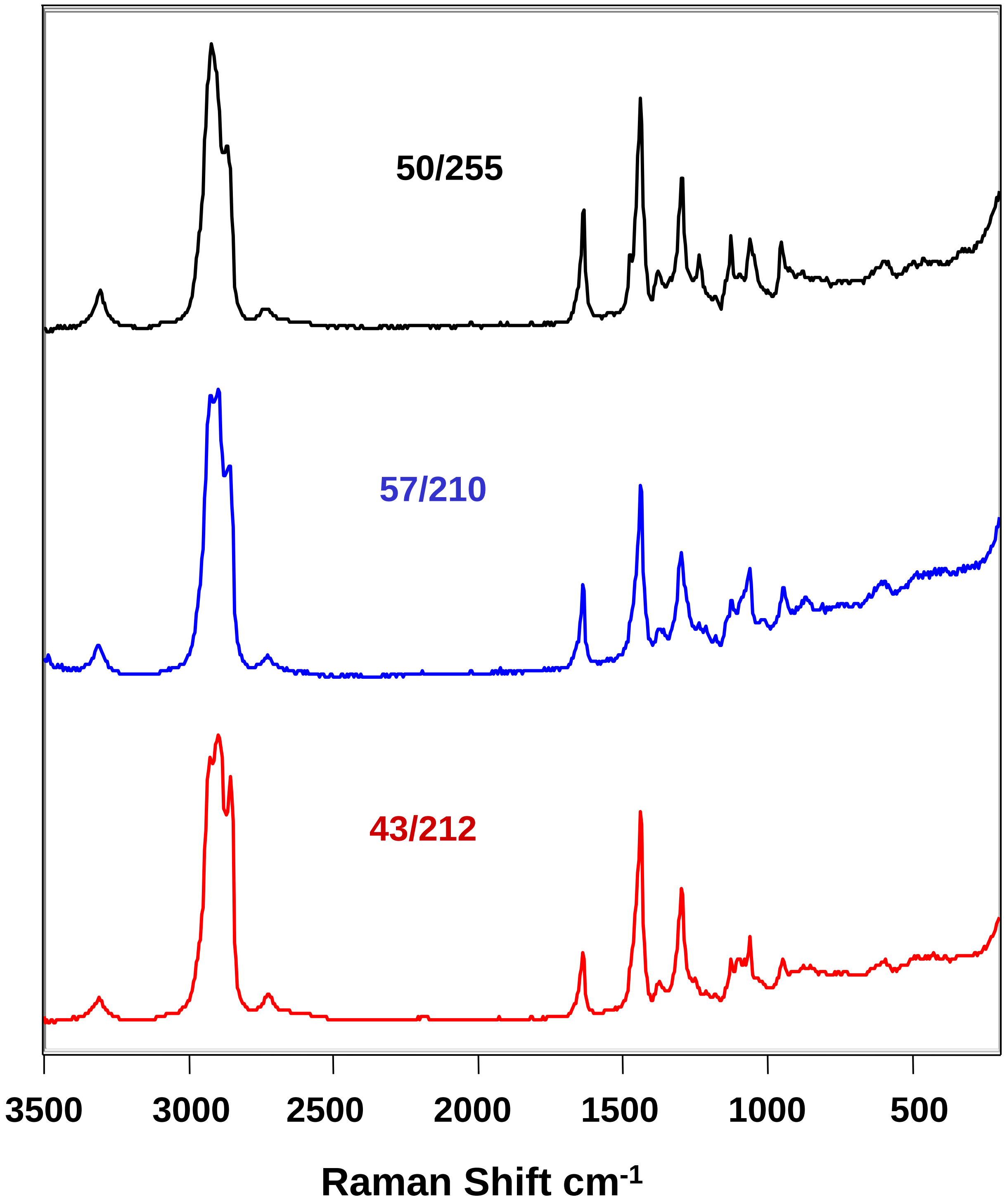
1) Identification

2) Quantitation

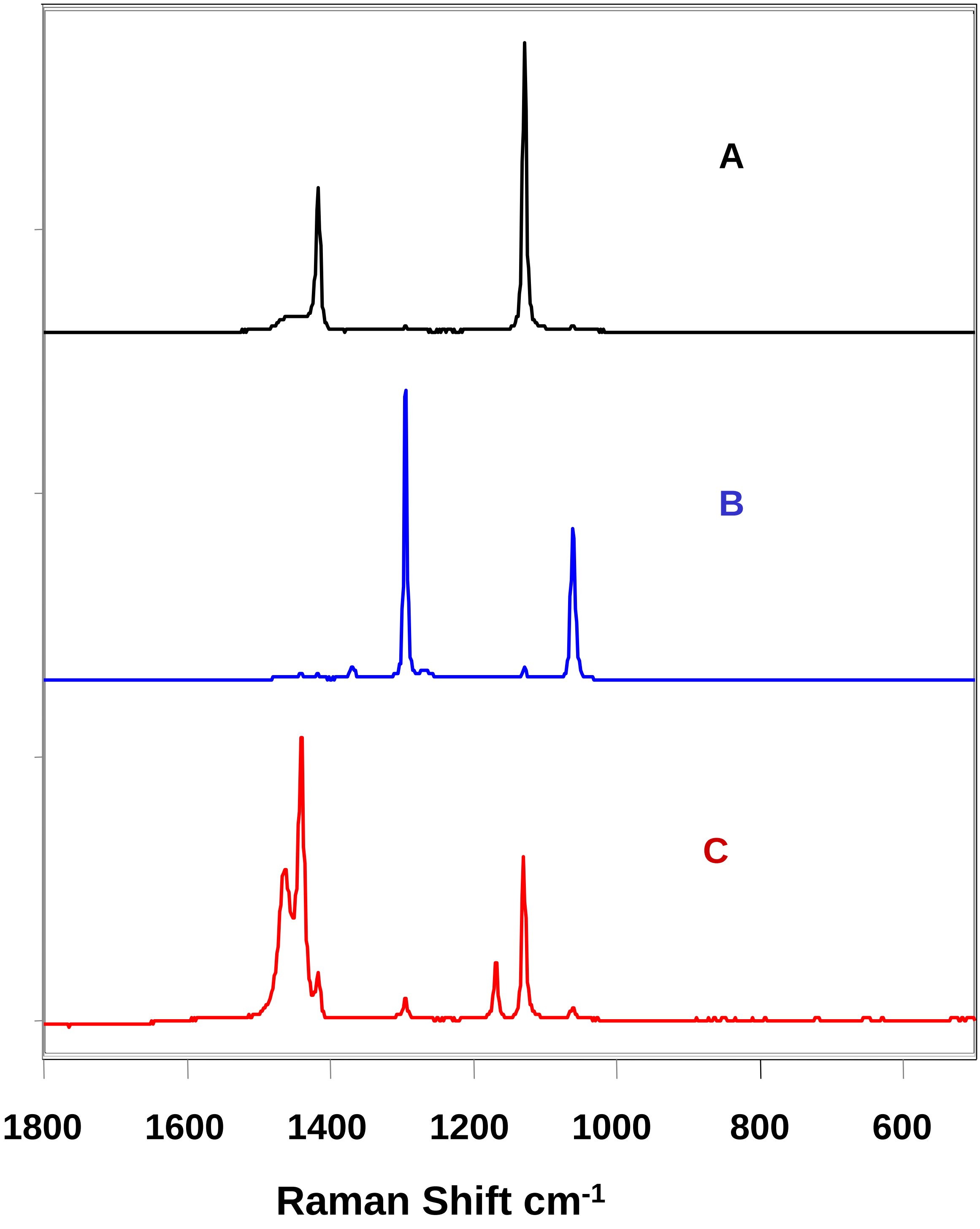
3) Structure/Property Studies



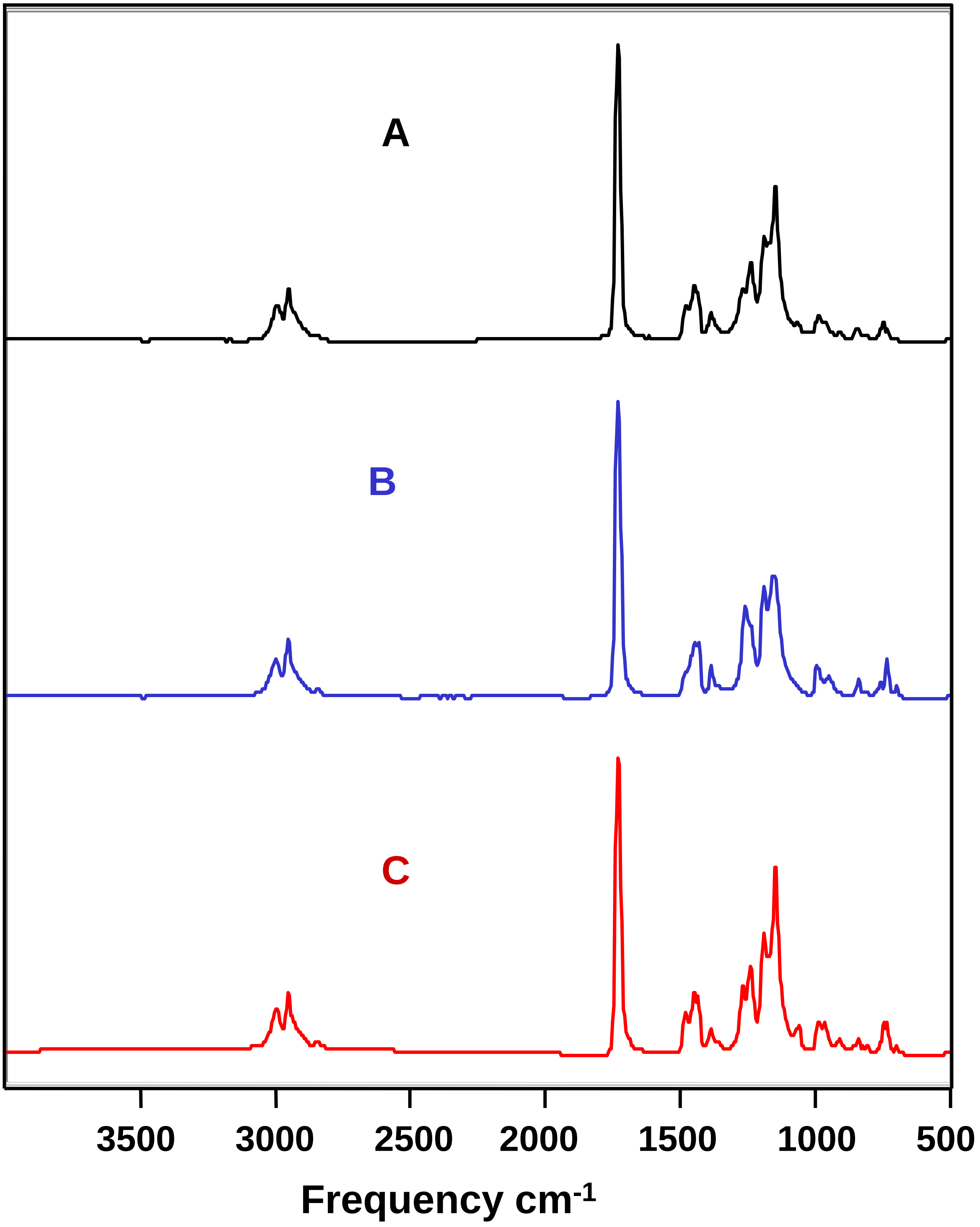
Infrared spectra of three different materials.
Glass transition temperatures and melt temperatures are listed.
These are clearly different but the IR spectra are quite similar.



The Raman spectra are also quite similar. Clearly there are molecular level effects occurring, which result in different macroscopic properties but are not clearly differentiated in the vibrational spectra at this level.



Here are three Raman spectra, which are quite different. Based on your understanding on the vibrational spectra of materials what structures might you assign these three spectra to? Answer in lecture!

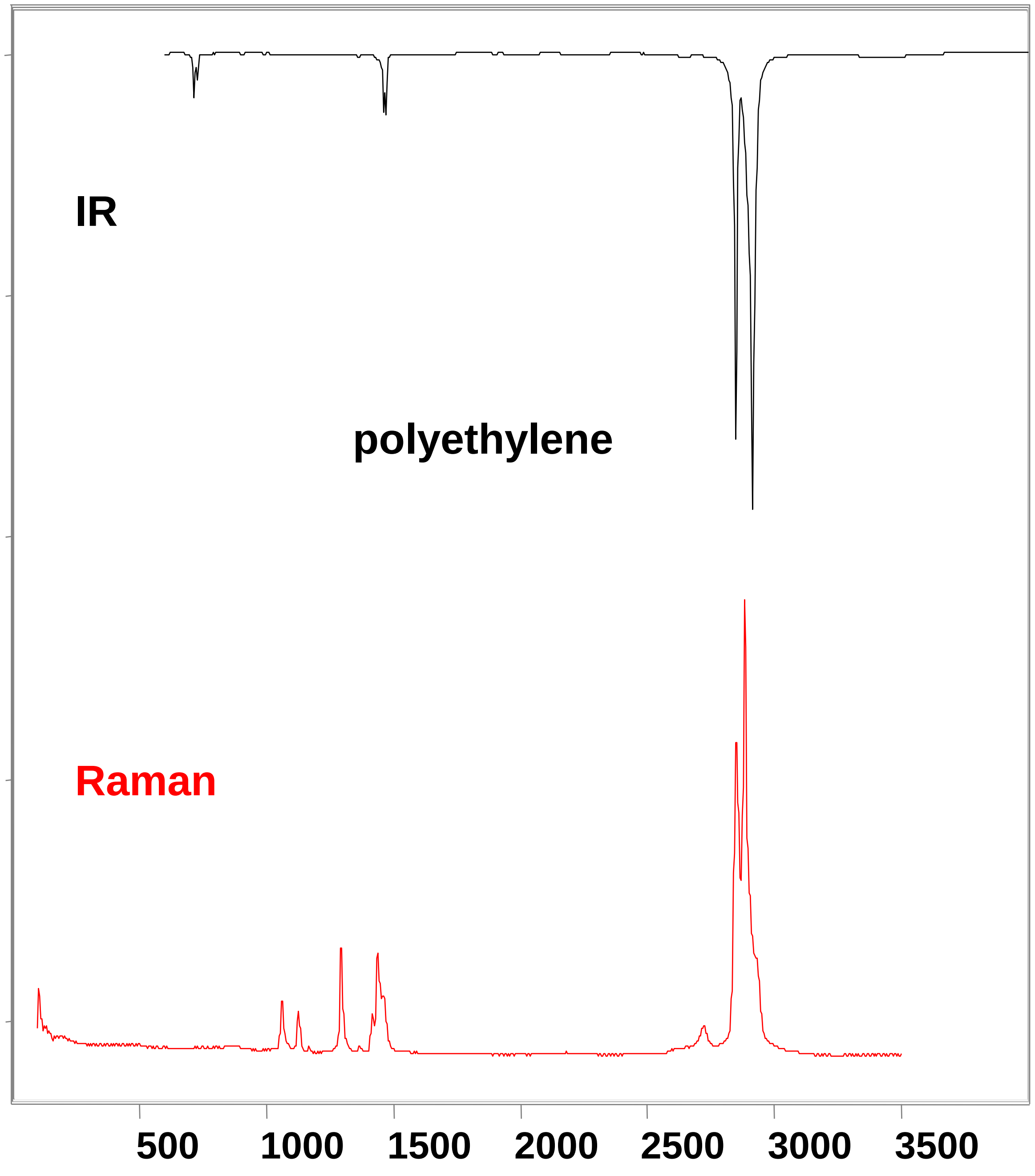


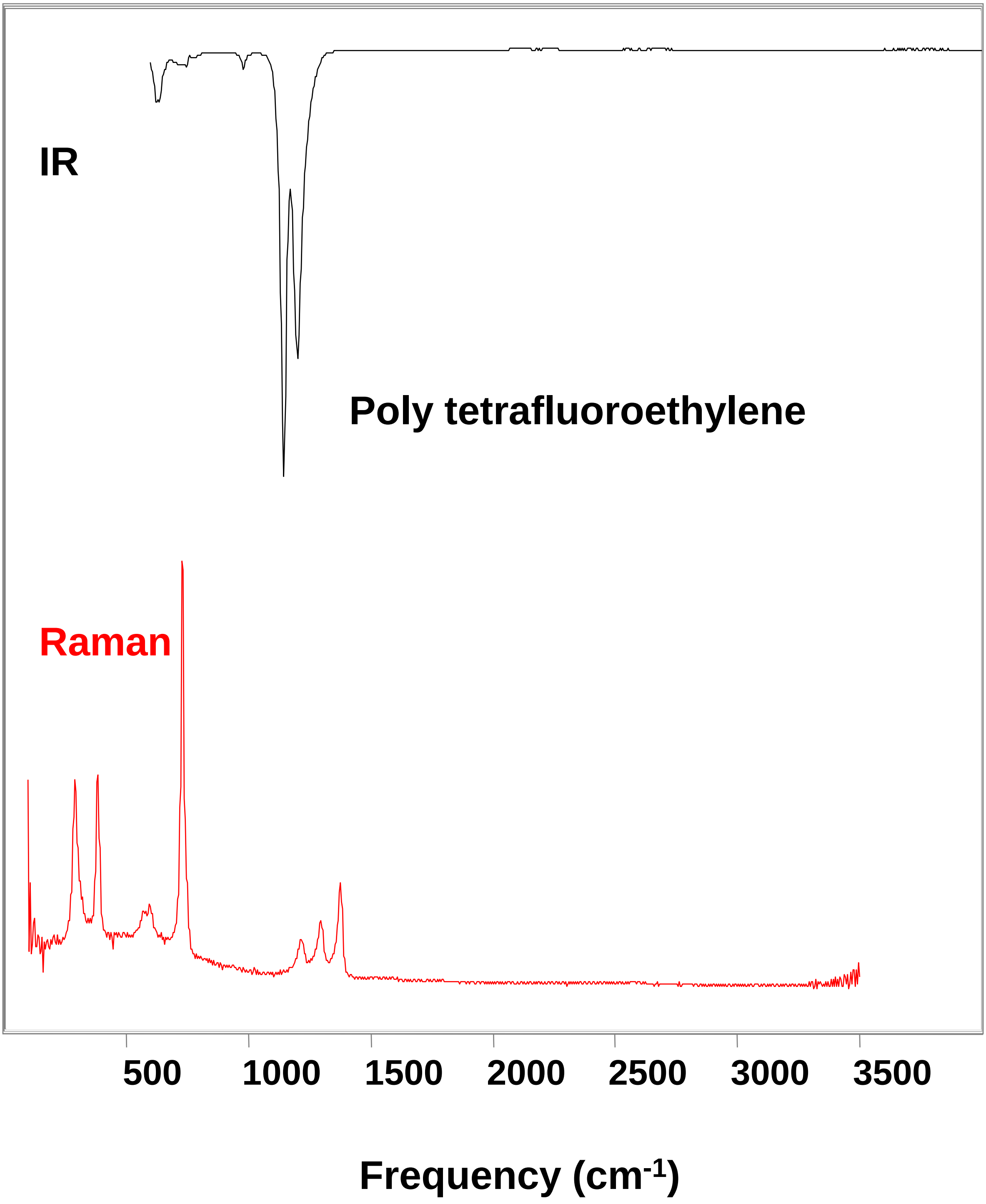
Finally here are three spectra of three materials. All have the same chemical formula but have slightly different material properties. These show the subtle effects introduced by stereospecificity or tacticity. As we proceed through this lecture we will see how subtle, not so subtle molecular structure effects are characterized through IR and Raman spectroscopy.

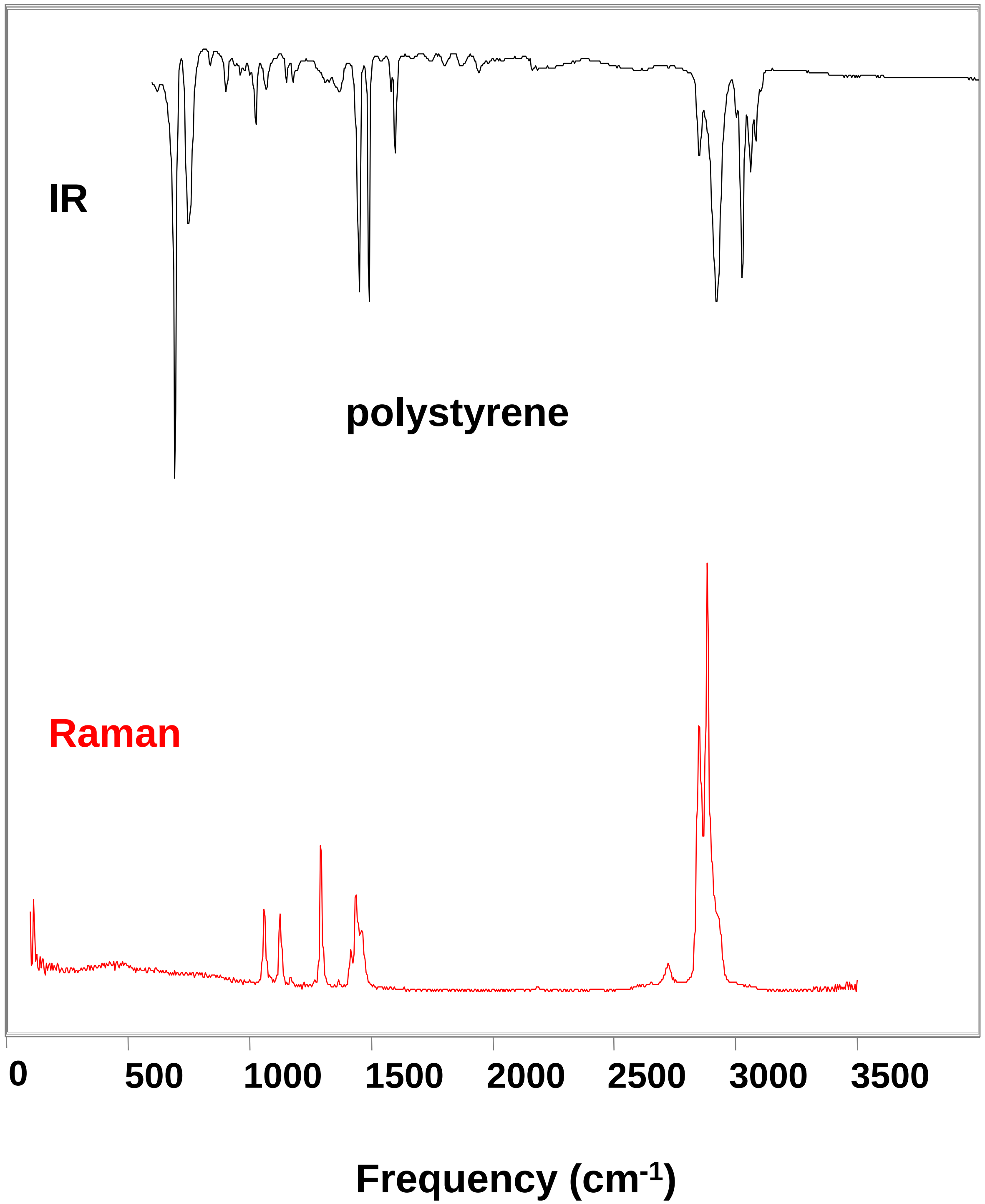
Polymer Structure

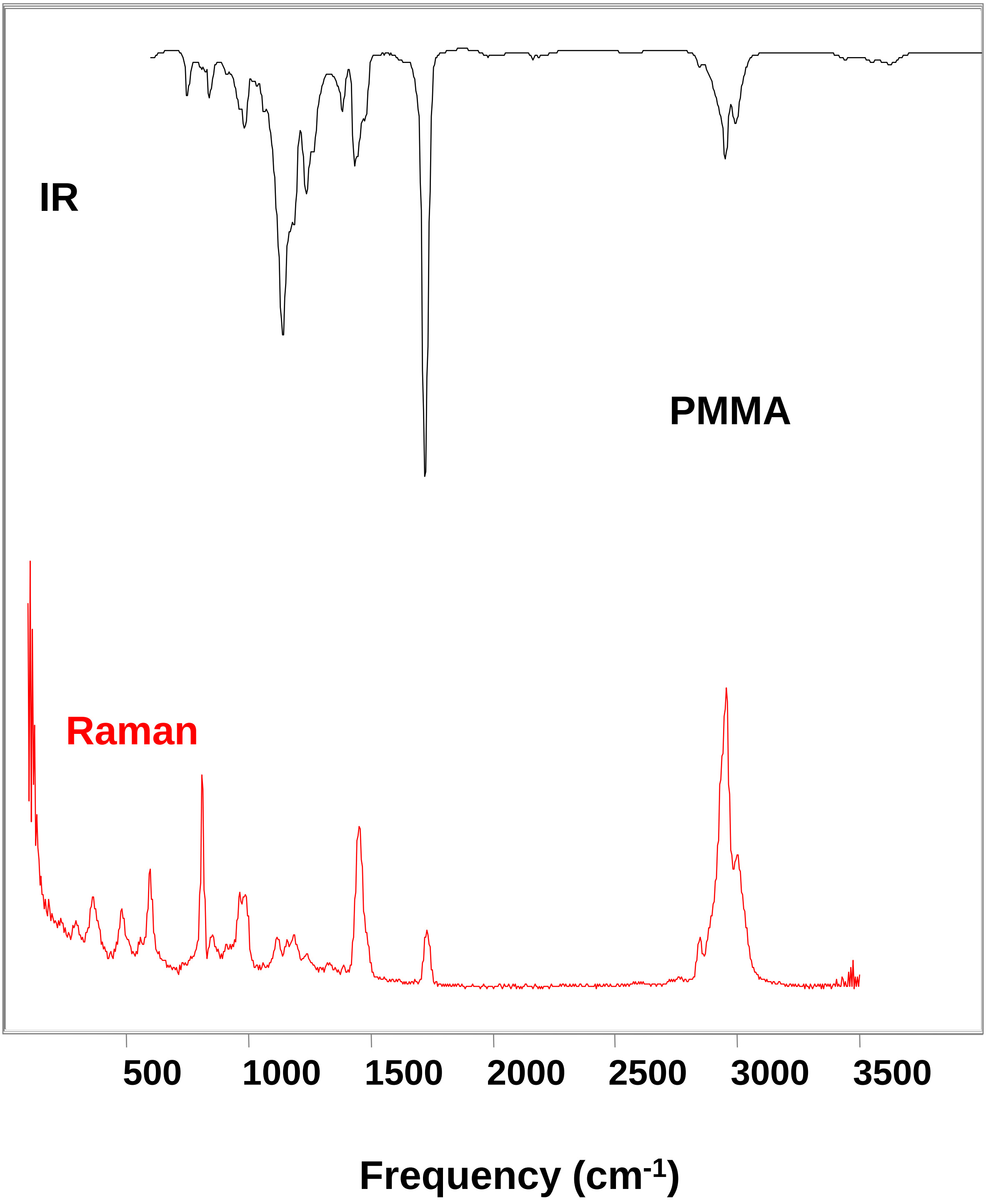
1. primary--chemical connectivity
    - composition
    - configuration
2. secondary--conformations
    - interconvertible
3. tertiary--crystallinity/orientation
    - morphology

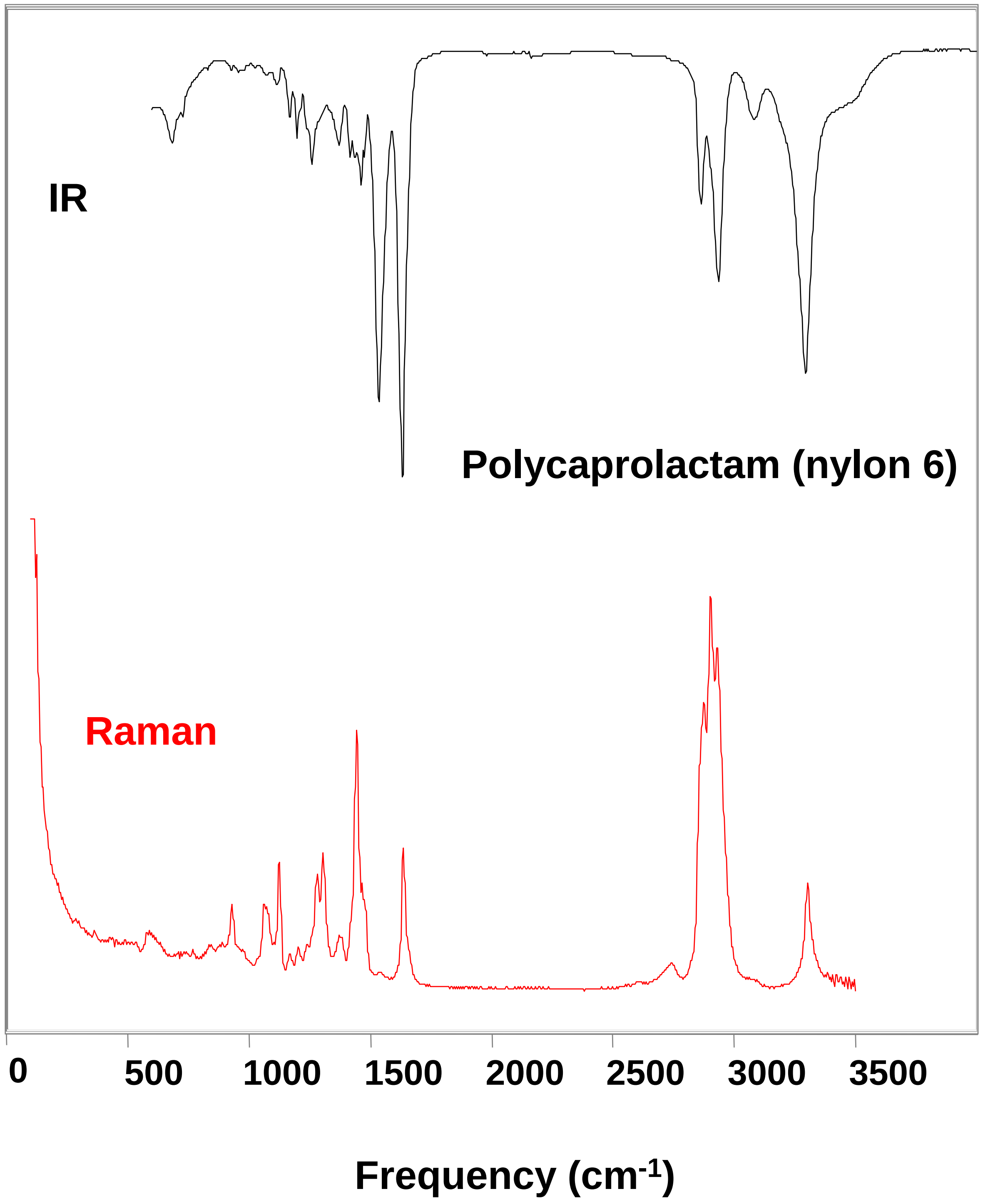
Vibrational spectroscopy has the potential to probe molecular level structure in all 3 levels. Primary structure is simply the functional groups present and their connectivity. Secondary structure involves conformational states such as trans/gauche conformations of methylene chains. Tertiary structure is the arrangement in space.

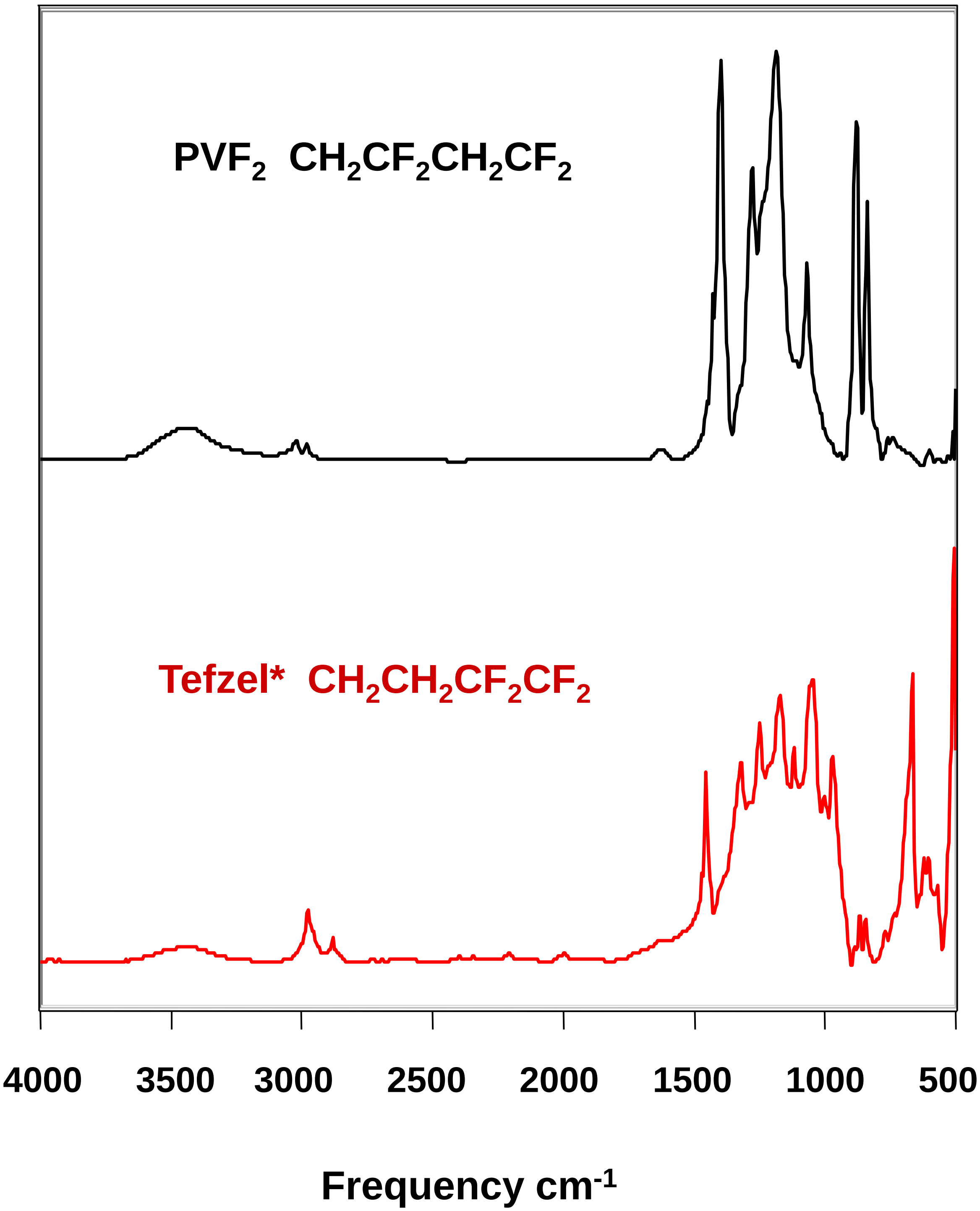

IR
polyethylene
Raman
500
1000
1500
2000
2500
3000
3500
Frequency (cm^{-1})


IR
Poly tetrafluoroethylene
Raman
500
1000
1500
2000
2500
3000
3500
Frequency (cm^{-1})

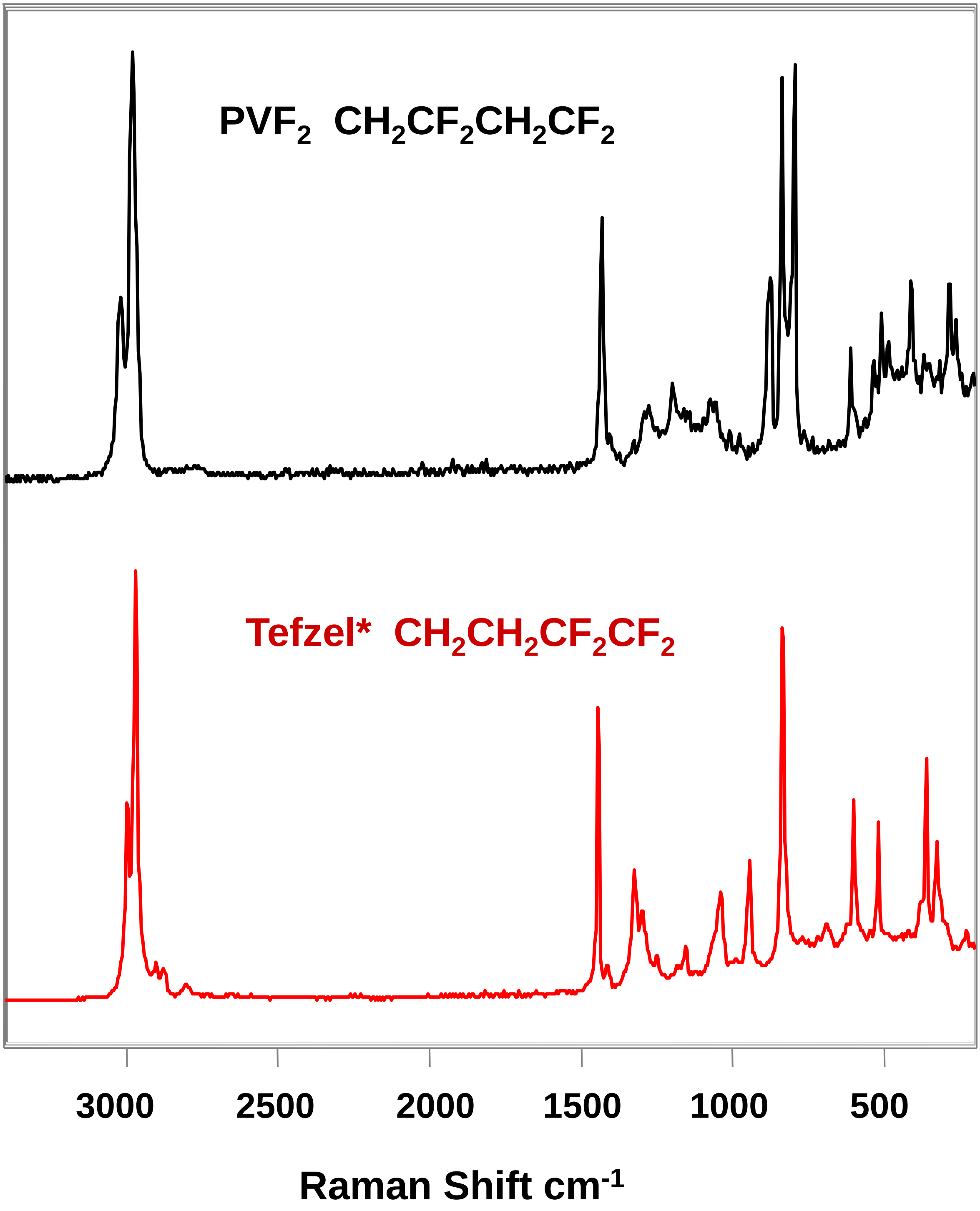

IR
polystyrene
Raman
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)


IR
PMMA
Raman
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)

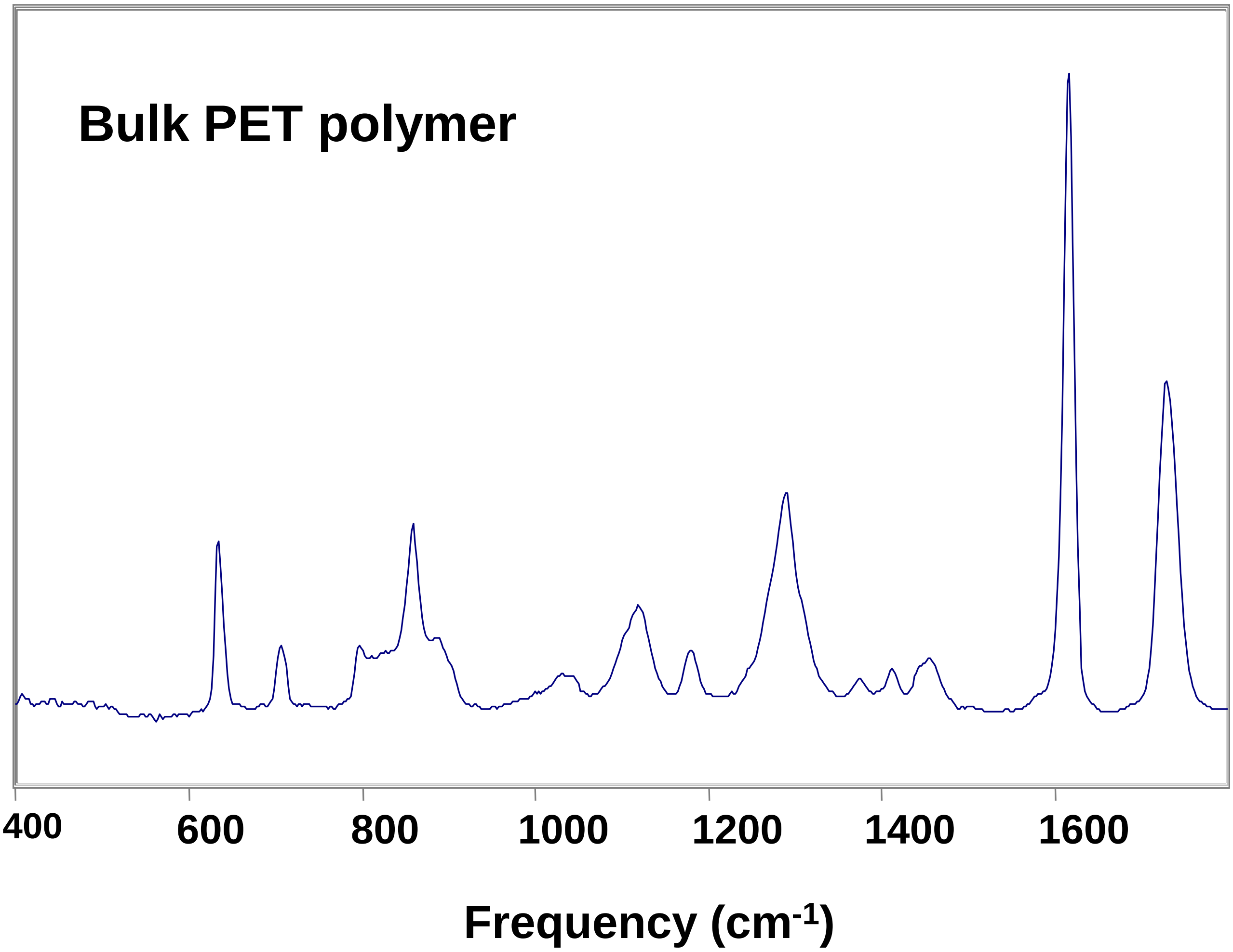

IR
Polycaprolactam (nylon 6)
Raman
0
500
1000
1500
2000
2500
3000
3500
Frequency (cm-1)



We actually have a case where a polymer can be prepared which is comprised entirely of defect structures. Tefzel® is the defect structure for PVF$_2$. As can be seen the infrared spectra for the two materials are quite different.

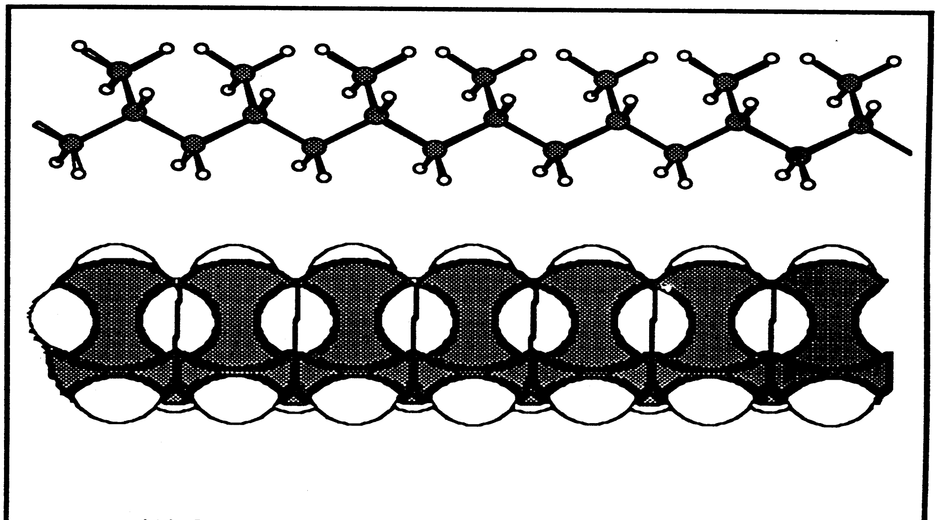


The Raman spectra also are quite different.

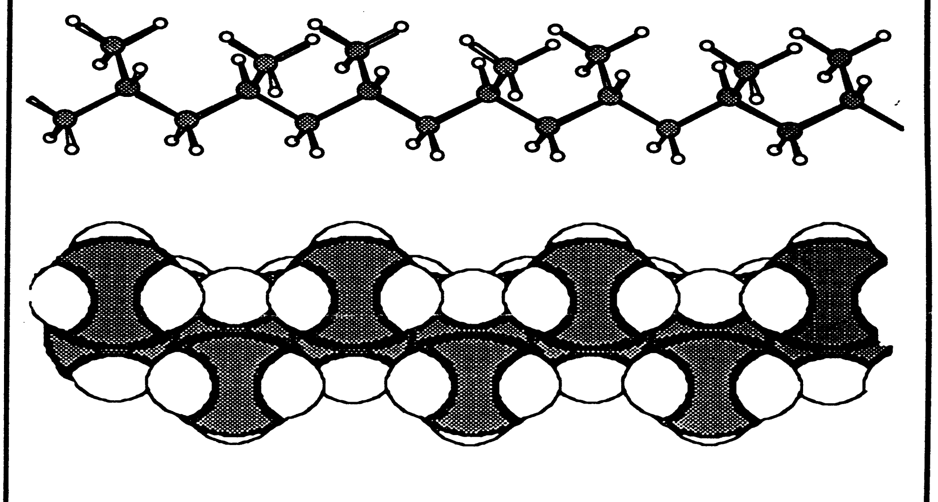


1725 cm^{-1}	C=O bandwidth	crystallinity
1000 cm^{-1}	O-CH_2/C-C	trans confomer
1096 cm^{-1}	C-O-C bend/C-C	trans confomer
1030 cm^{-1}	O-$_{CH2}$/C-C	gauche confomer

Polymer Microstructure 11



(A) Part of an Isotactic Polypropylene Molecule

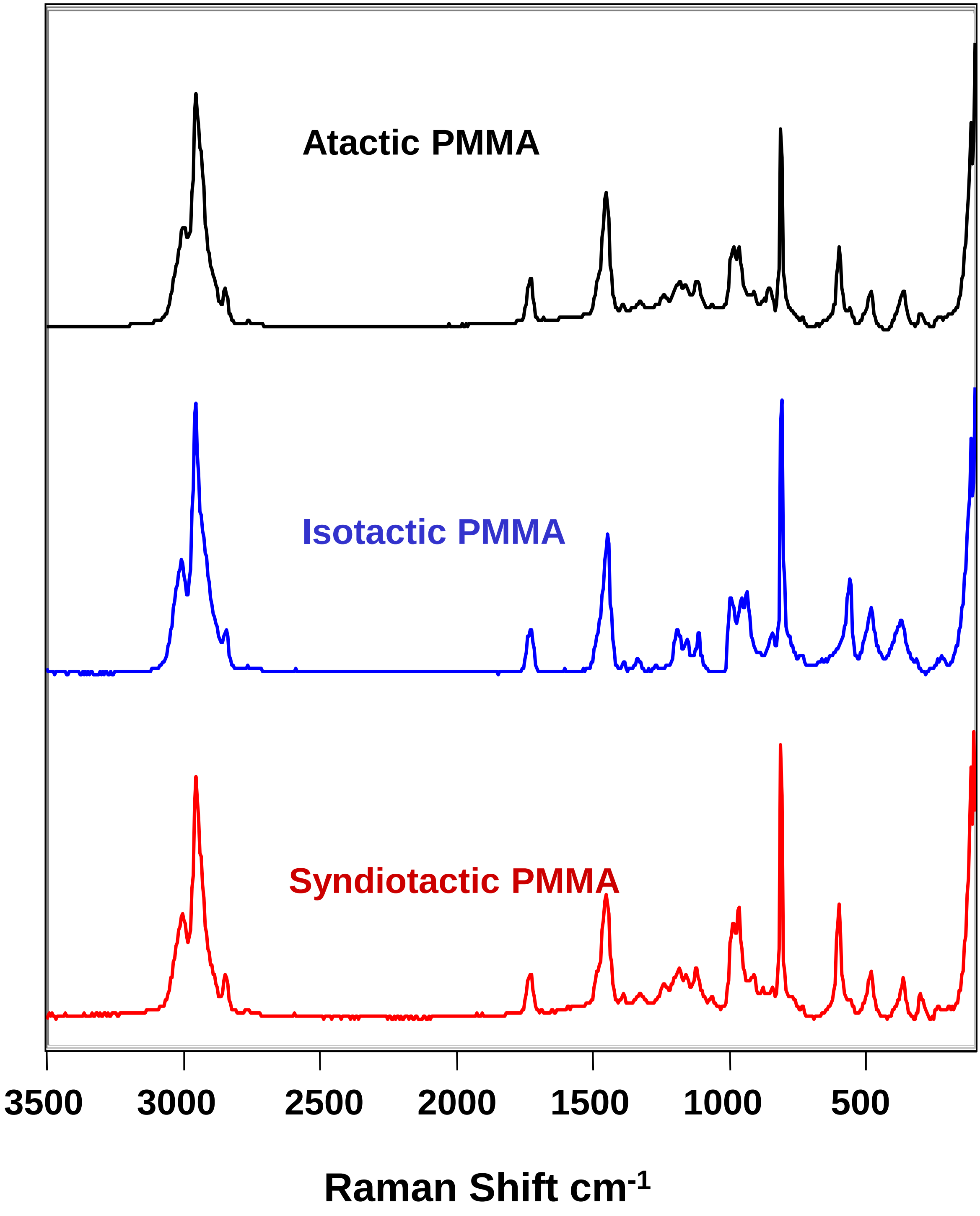


(B) Part of a Syndiotactic Polypropylene Molecule

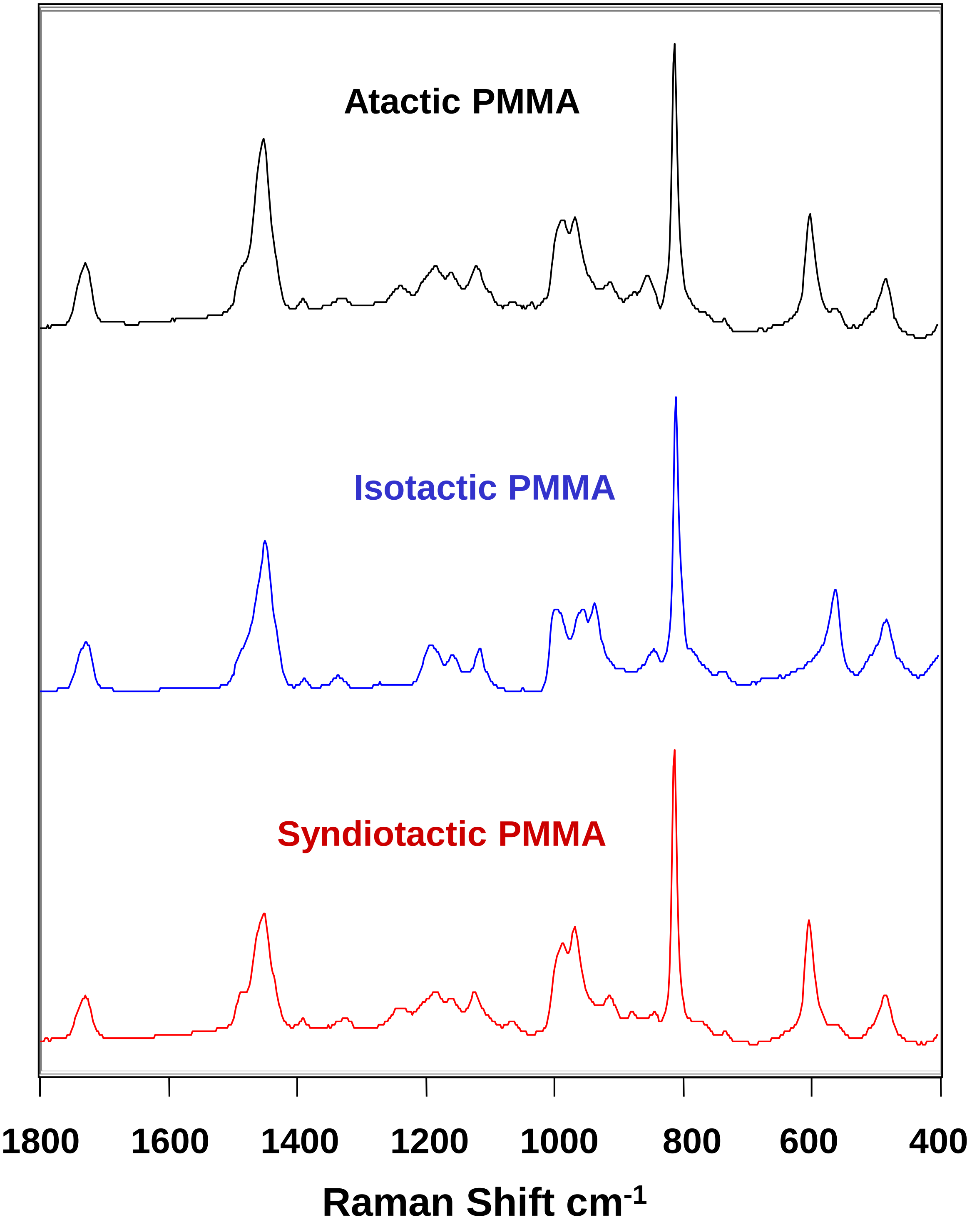
Figure 1.6 *Side view "ball and stick" and top view space filling models of extended chain isotactic and syndiotactic polypropylenes.*

Figure 1.6 "Fundamentals of Polymer Science"

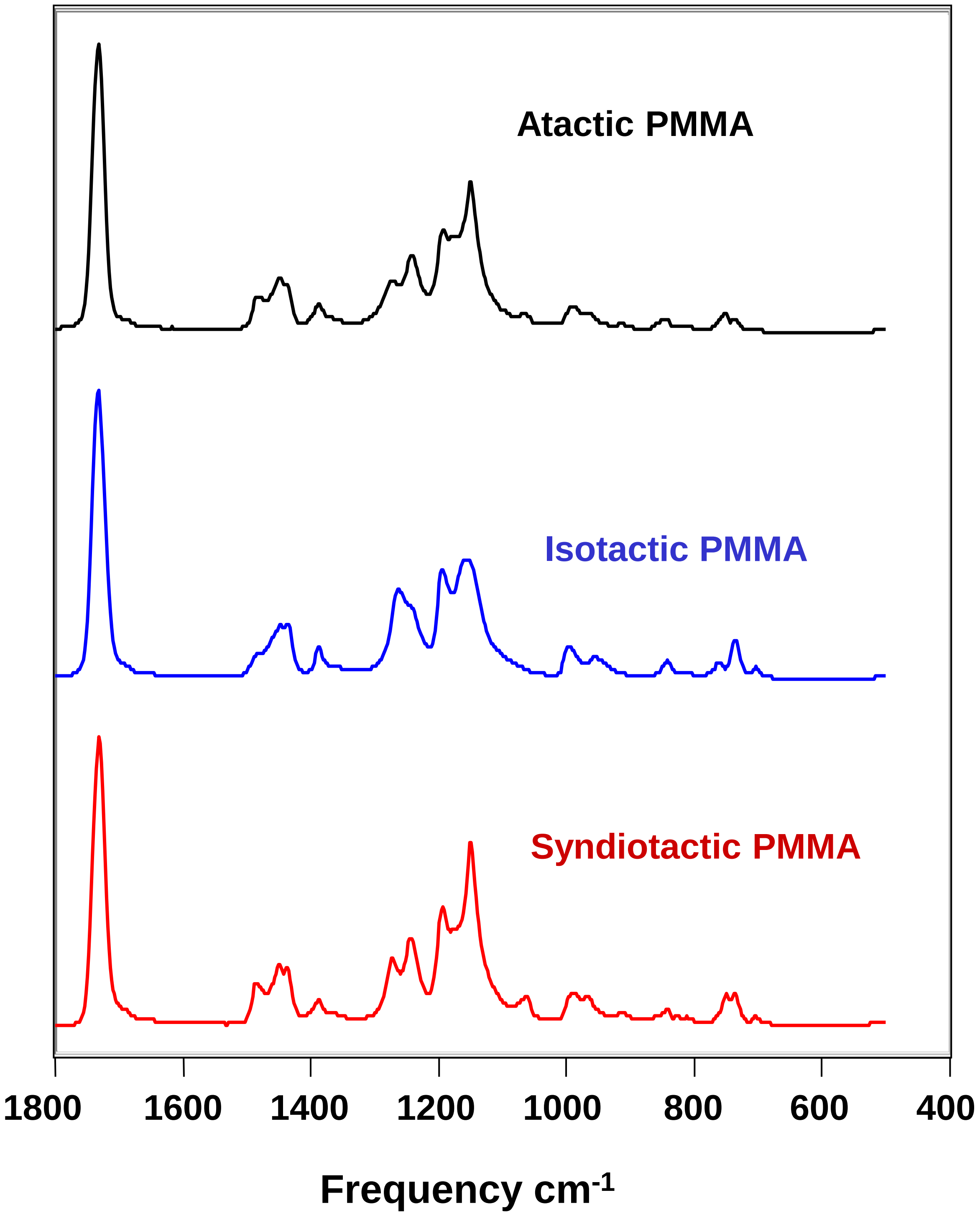
Tacticity is the way monomers are arranged spatially in the polymerization process. Atactic have a random arrangement, isotactic have all the pendant groups coming off of the same side, and syndiotactic have a regular alternation. These different arrangements of side groups can clearly impact how polymer chains pack together, but since vibrational modes are usually localized, the arrangement of a neighboring repeat unit has only a small effect on the spectrum.



For PMMA the only real difference between the spectra is that the atactic sample has slightly broader spectral features. This arises from the poor packing which occurs with the random orientation of the side groups. The syndiotactic and isotactic probably have slightly higher degrees of crystallinity arising from better chain packing.



Similar effects are observed in the Raman spectra.


Atactic PMMA
Isotactic PMMA
Syndiotactic PMMA
1800
1600
1400
1200
1000
800
600
400
Frequency cm-1

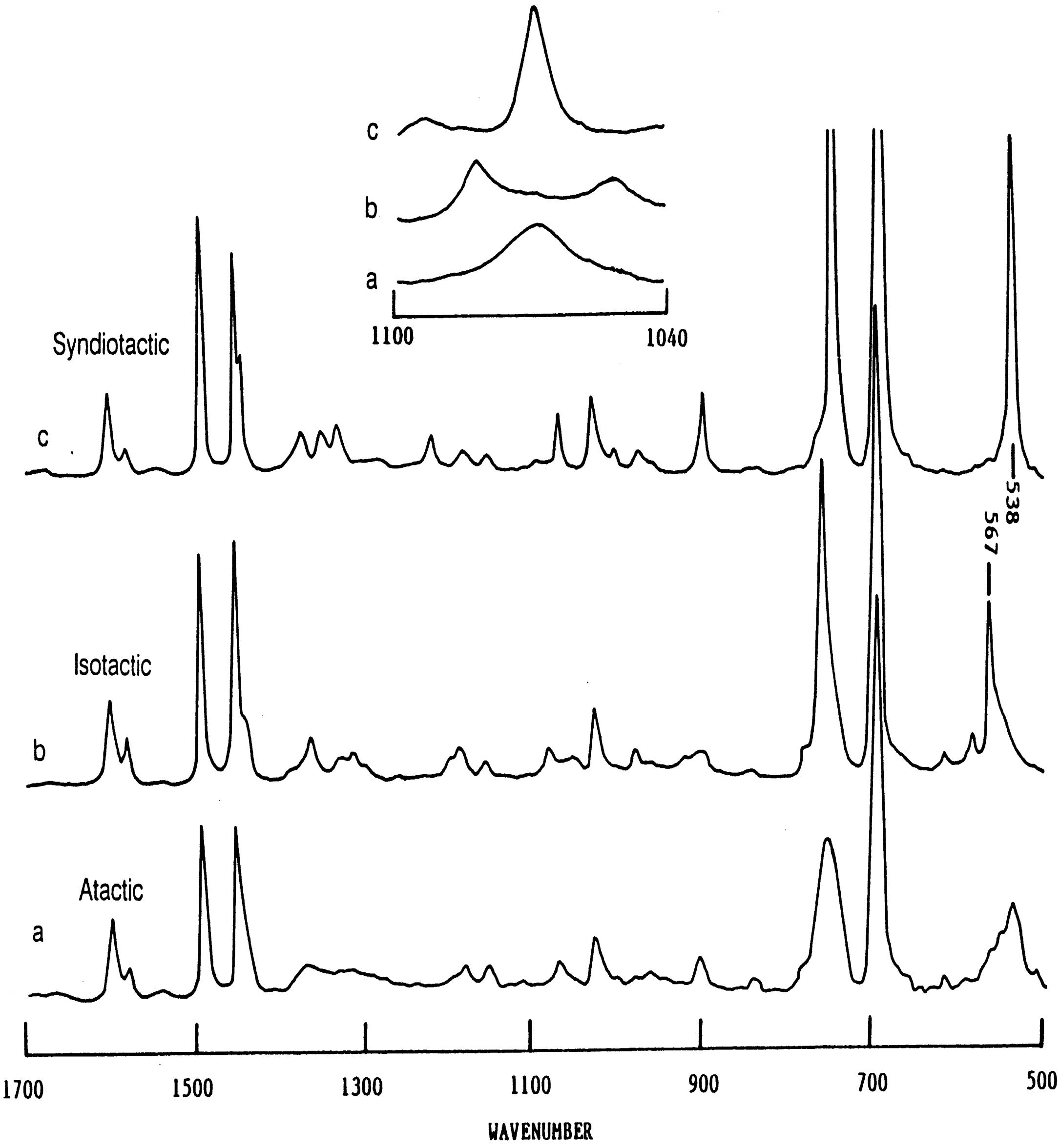


Figure 4.13. IR spectra of atactic (a), isotactic (b), and syndiotactic (c) polystyrene. (Reproduced from reference 8. Copyright 1989 American Chemical Society.)

Figure 4.13 “Spectroscopy of Polymers”

There are very subtle differences which can be used to differentiate the three samples as shown in the inset. In the C-C stretching region the spectra are different.

Conformation/Crystallinity

Conformation--energetically close states accessible
by rotation around single bonds
trans/gauche interconversion

Crystallinity--regular three dimensional arrangement
of polymer chains, where chains (molecules)
are crystallagraphically equivalent

Vibrational spectroscopy is sensitive to the former and relatively insensitive to the latter!

This is an important point to remember and which we will continue to emphasize. Vibrational spectra are sensitive to the conformational states, which accompany crystalline order. They are not directly sensitive to crystallinity. If one could arrange to have the same conformational state populations in an amorphous sample as in a crystalline sample, the spectra could be indistinguishable.

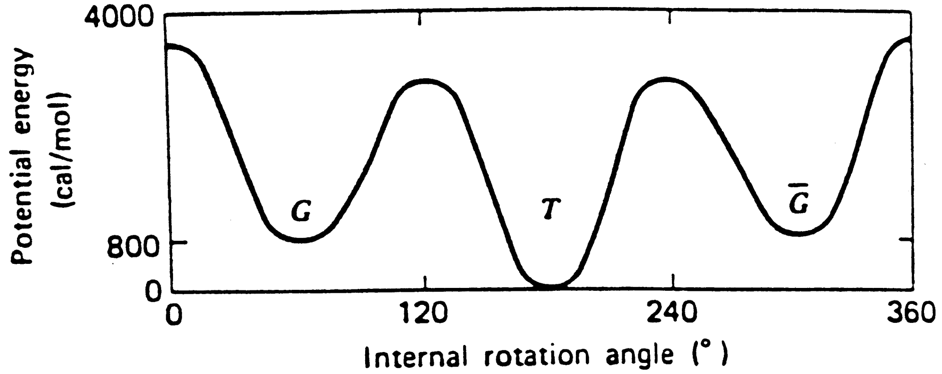
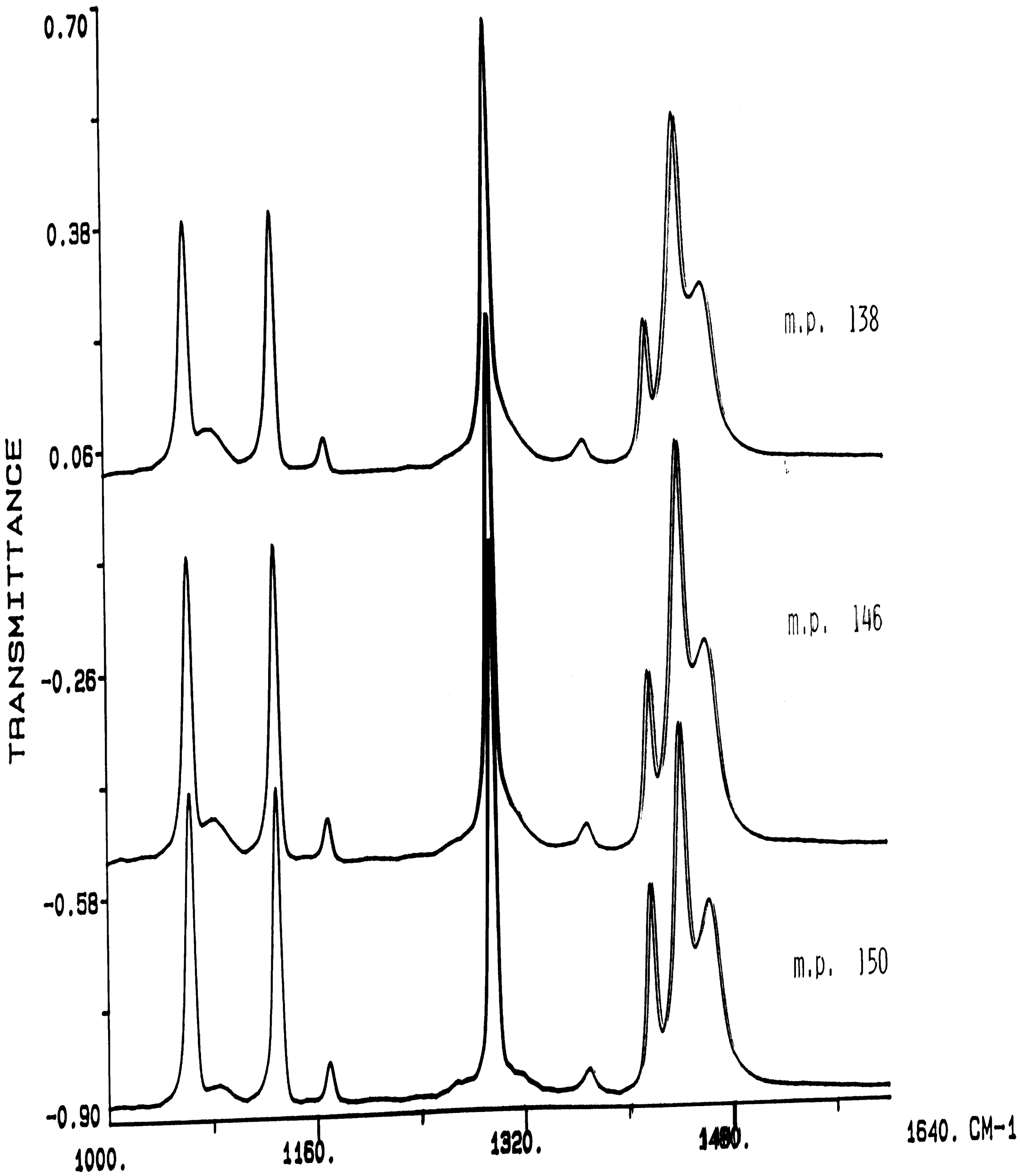


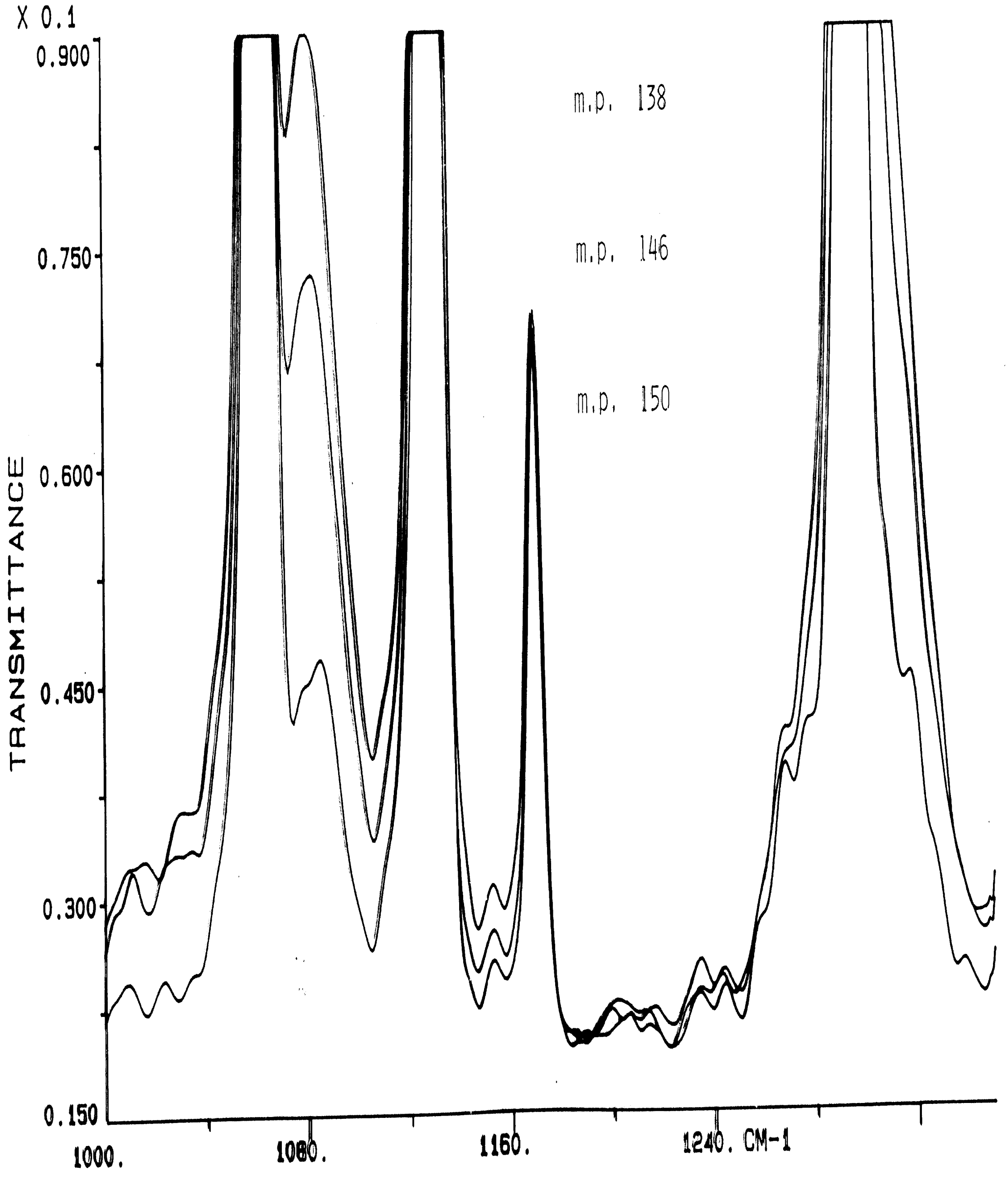
Figure 4.14. Potential energy curve for internal rotation about the C – C bond of butane. (Reproduced with permission from reference 11. Copyright 1979 J. L. Koenig.)

Figure 4.14 "Spectroscopy of Polymers"

Conformational states can be interconverted through rotations around single bonds. While this does require some energy to overcome potential barriers, it can occur. So material which starts out as non-crystalline can through thermal treatments become crystalline. Similarly, one can disrupt crystalline structures through appropriate heating to the melt.



These are Raman spectra of three different polyethylenes with varying melting points. The higher the melting, presumably the more crystalline the polymer is. There is a conformationally sensitive band at 1080 cm^{-1} which has been assigned to gauche conformers.



In this scale expanded view, one can clearly distinguish the gauche conformer population decreasing as the melting index goes up. While it is likely that the polyethylene is becoming more crystalline, this data shows only the shift in relative conformer populations.

Poly ethylene terephthalate

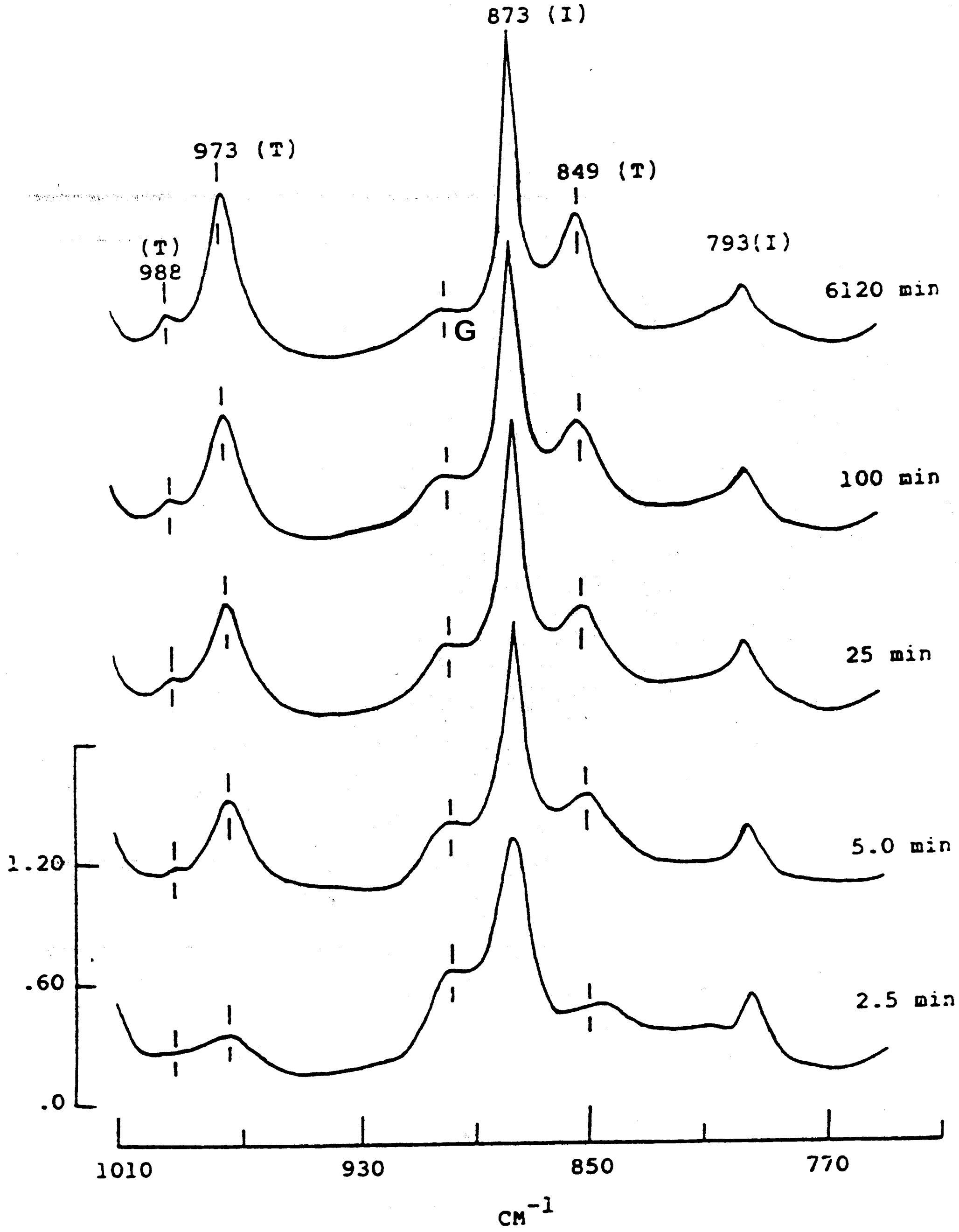
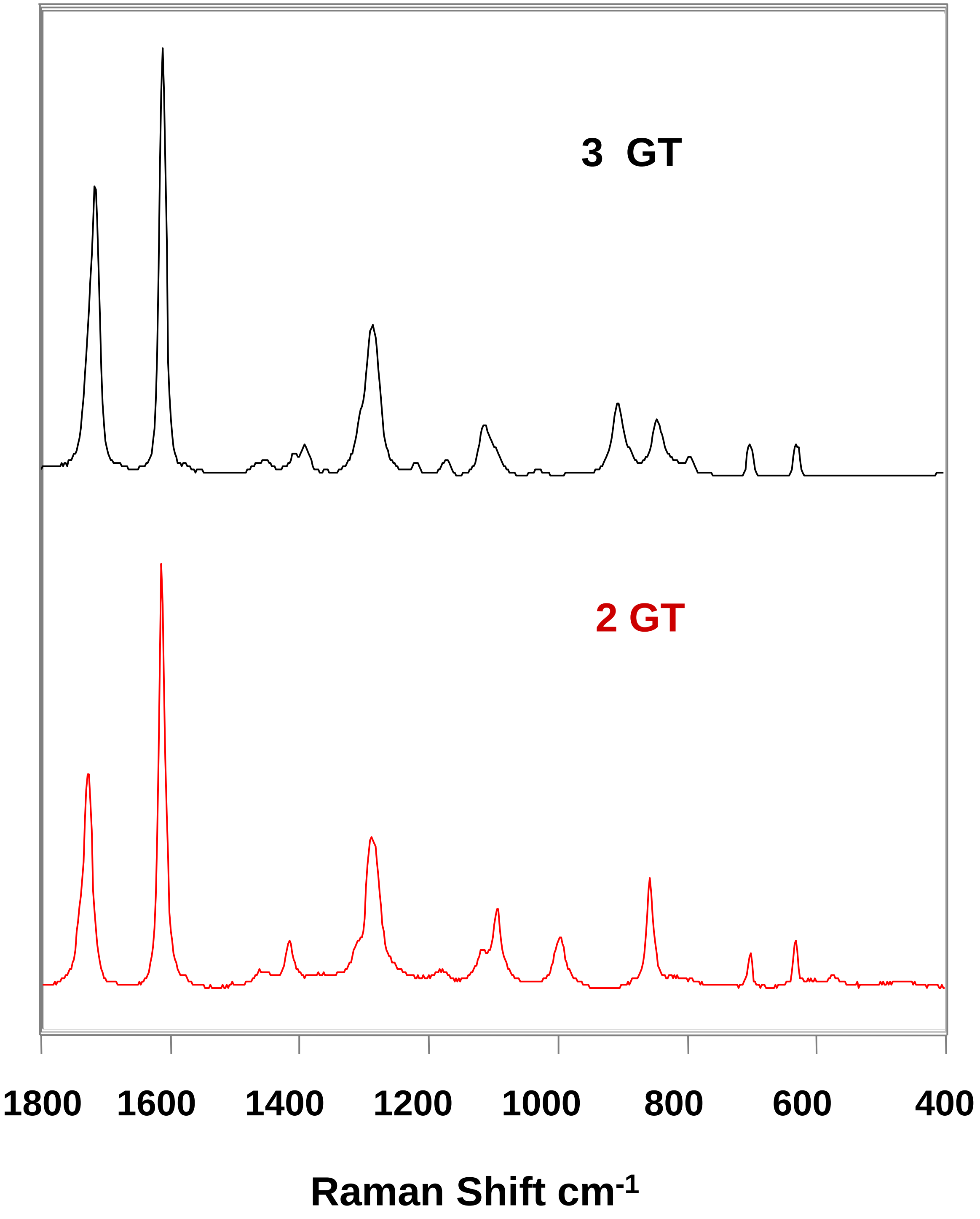
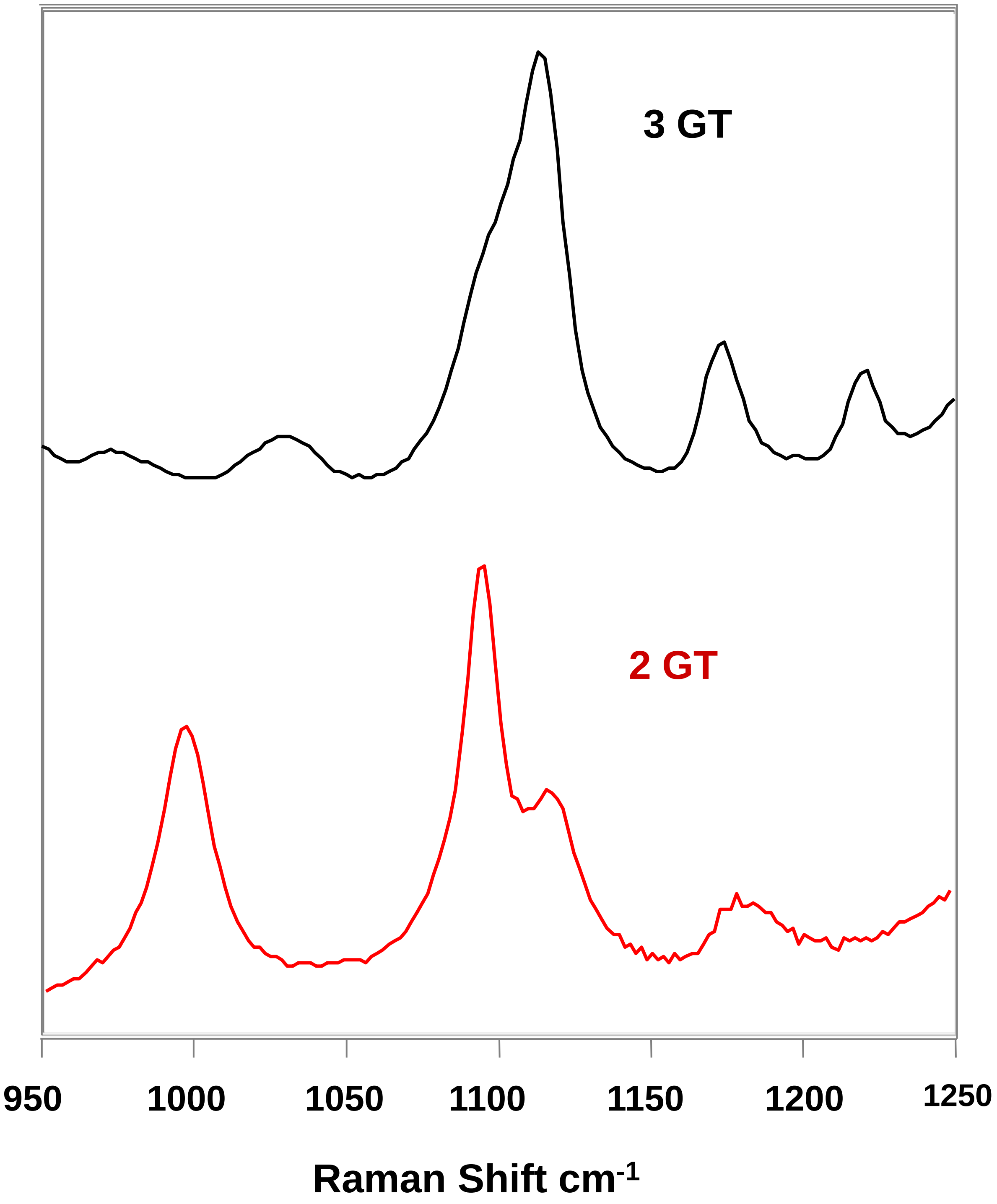


Figure 3.24 “Spectroscopy of Polymers”

In polyethylene terephthalate (PET) development of the crystalline state requires that the methylene chains adopt a trans conformation. Thermal annealing treatment provides the energy and time for the barrier crossing discussed earlier and gradually gauche converts to trans as seen by the increase in intensity of the bands at 849 cm^{-1} and 973 cm^{-1} in the infrared spectrum.



The difference between 2GT (polyethylene terephthalate) and 3GT (polypropylene terephthalate) is the addition of a methylene linkage in the aliphatic chain. There are significant differences in the spectra, since 2GT crystallizes as a zig-zag chain while 3GT crystallizes as a helix.



Helix formation requires gauche conformations in the methylene segments. Thus the “crystalline sensitive bands” for 3GT are actually the gauche bands. One can not assume that all crystalline forms involve trans structures.

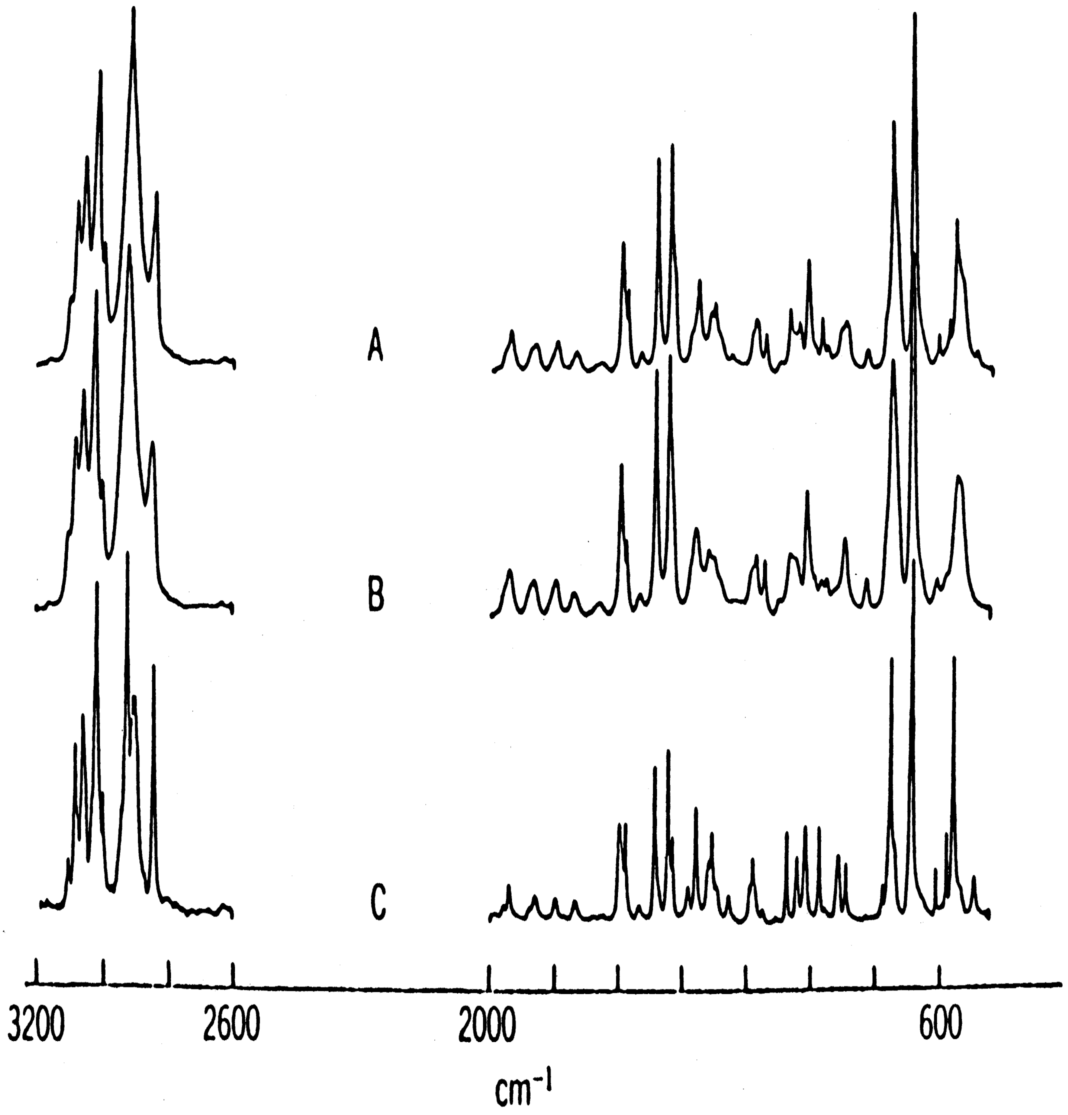


Figure 6.7 The infrared spectrum of isotactic polystyrene. (A) Annealed, (B) quenched from the melt, and (C) difference spectrum (A - B).

Figure 6.7 “Fundamentals of Polymer Science”

In general, crystalline spectra are characterized by sharper features than those found in amorphous samples. This is due to the restricted numbers of environments encountered in a crystal. Since any vibrational mode is slightly affected by the surrounding environment, an amorphous system, with a large number of varying environments will tend to have more diffuse infrared and Raman spectra.

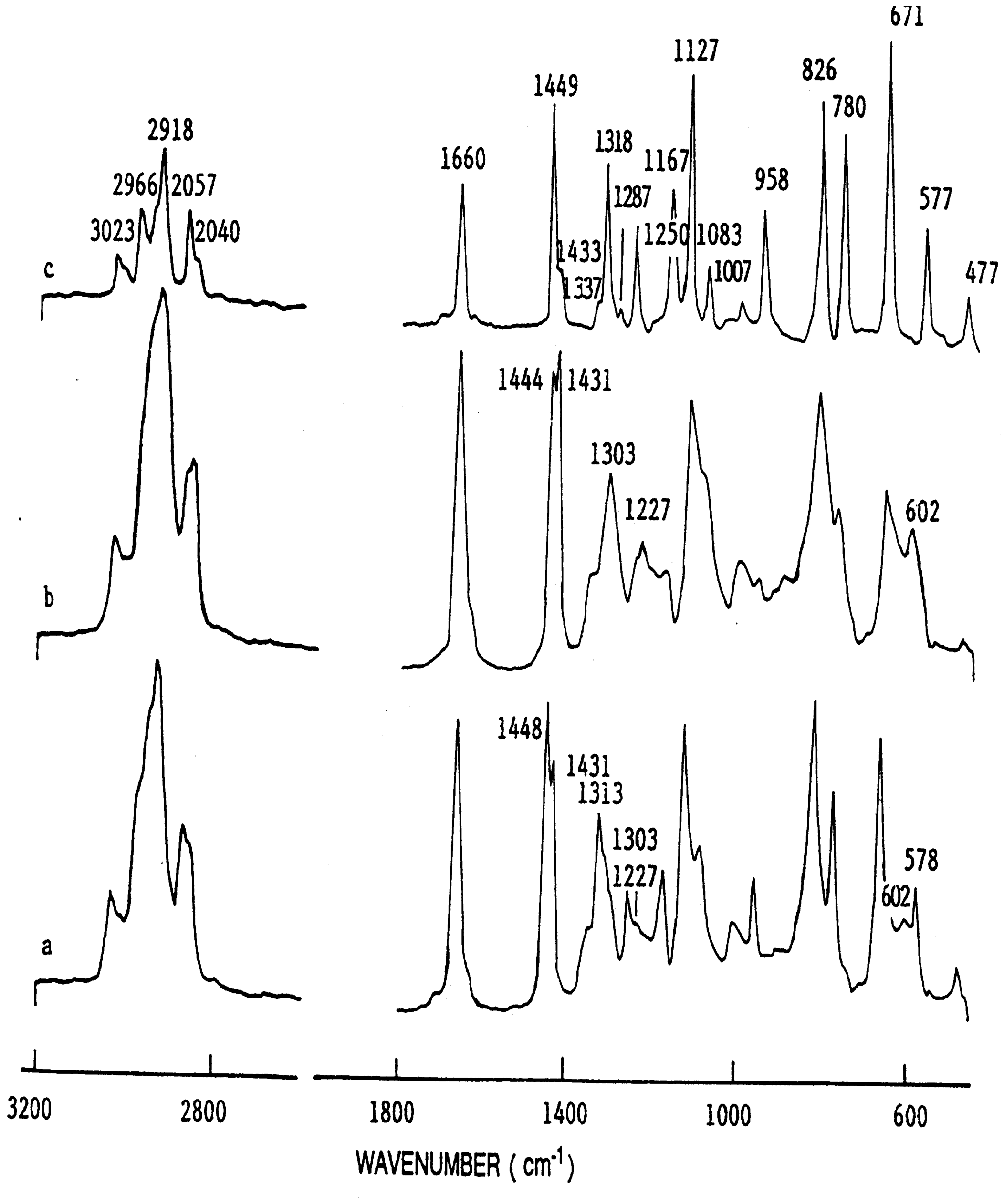


Figure 3.16. The spectrum of a cast film of predominately (>90%) trans-1,4-polychloroprene polymerized at −20 °C (spectrum a) is compared with the same sample heated to 80 °C (above the melting point) for 15 min (spectrum b). The "purified" crystalline isomer spectrum (spectrum c) exhibits the sharp band structure expected for a regular crystalline array. (Reproduced with permission from reference 48. Copyright 1974 John Wiley Sons, Inc.)

Figure 3.16 "Spectroscopy of Polymers"

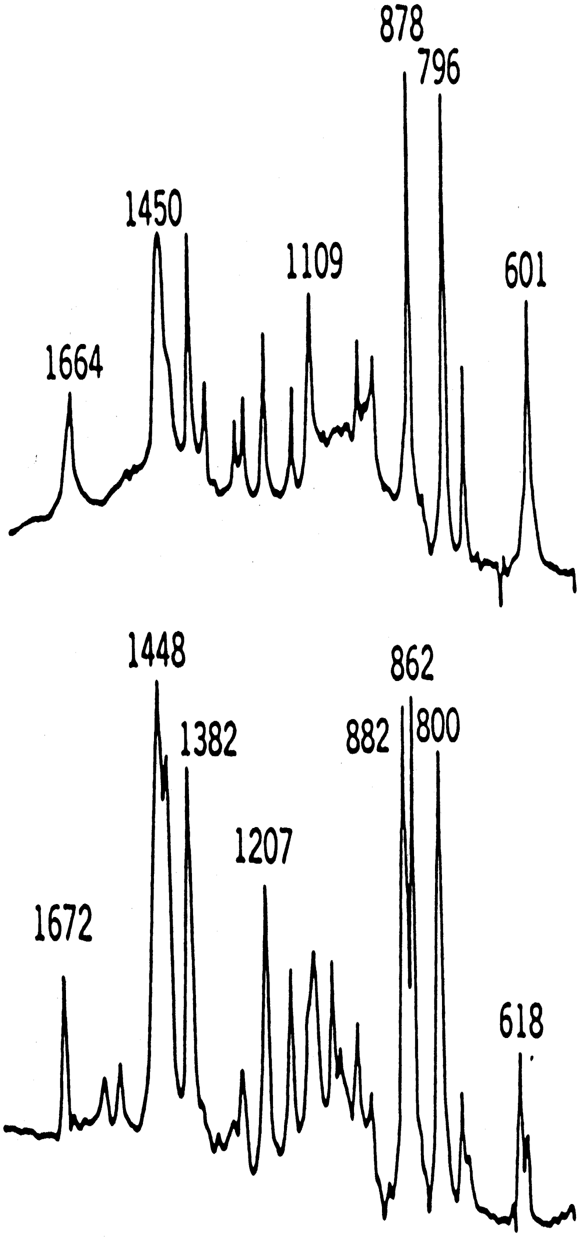


Figure 6.8 The infrared spectrum of the α (bottom) and β (top) crystalline forms of trans-*1,4-polyisoprene.*

Figure 6.8 “Fundamentals of Polymer Science”

In some cases, there can actually be several energetically similar crystalline states each with sharp spectra that differ from each other.

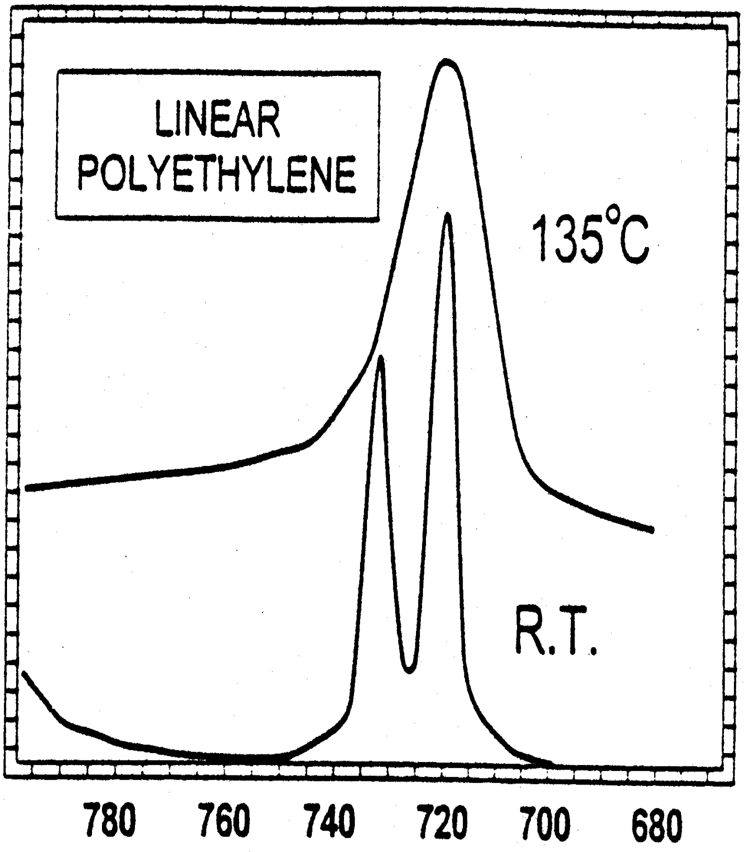


Figure 19

There is only one case that we know of where the spectra show features that are truly due to crystalline effects and not just conformational and environmental effects. In polyethylene which has been crystallized several bands actually show crystal field splitting. This occurs when the vibrational modes on adjacent chains interact and cause the splitting of the energy states. Why doesn't this occur in other systems? Think of which polymer chains one could pack close enough together to actually observe chain-chain interactions.

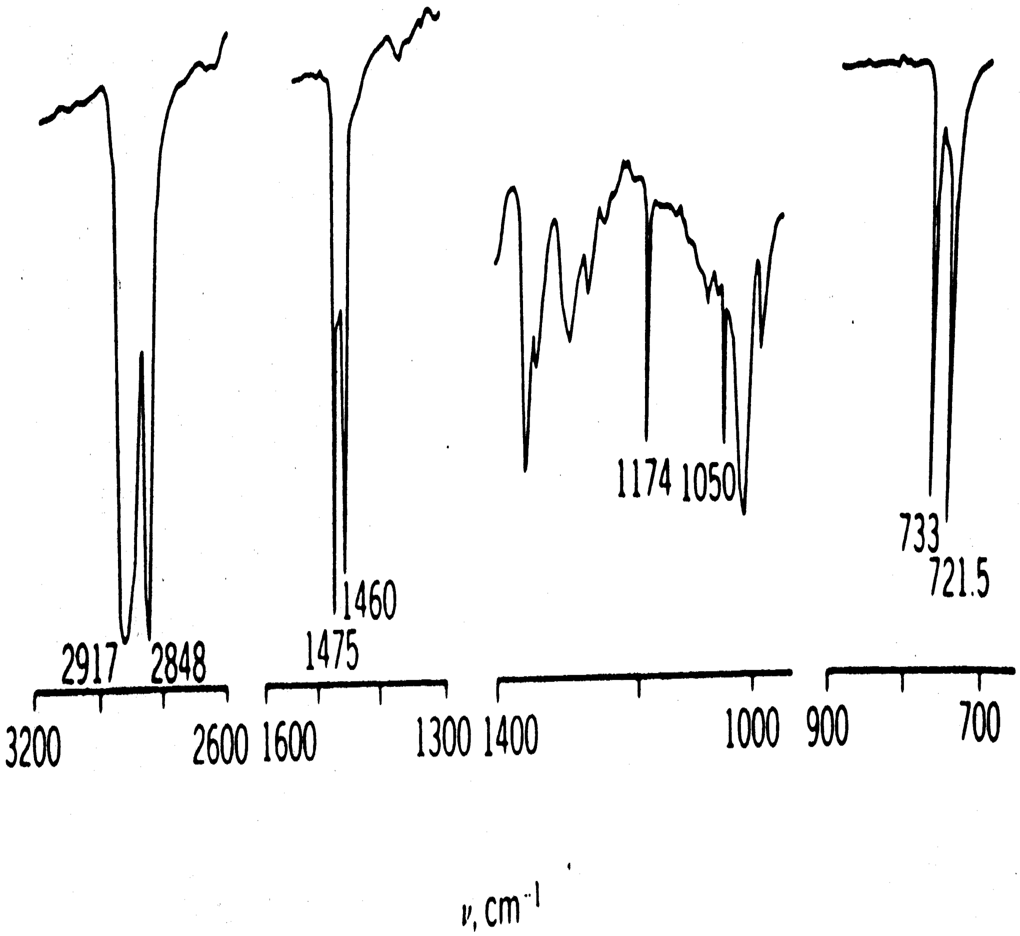


Figure 6.10 The infrared spectrum of polyethylene.

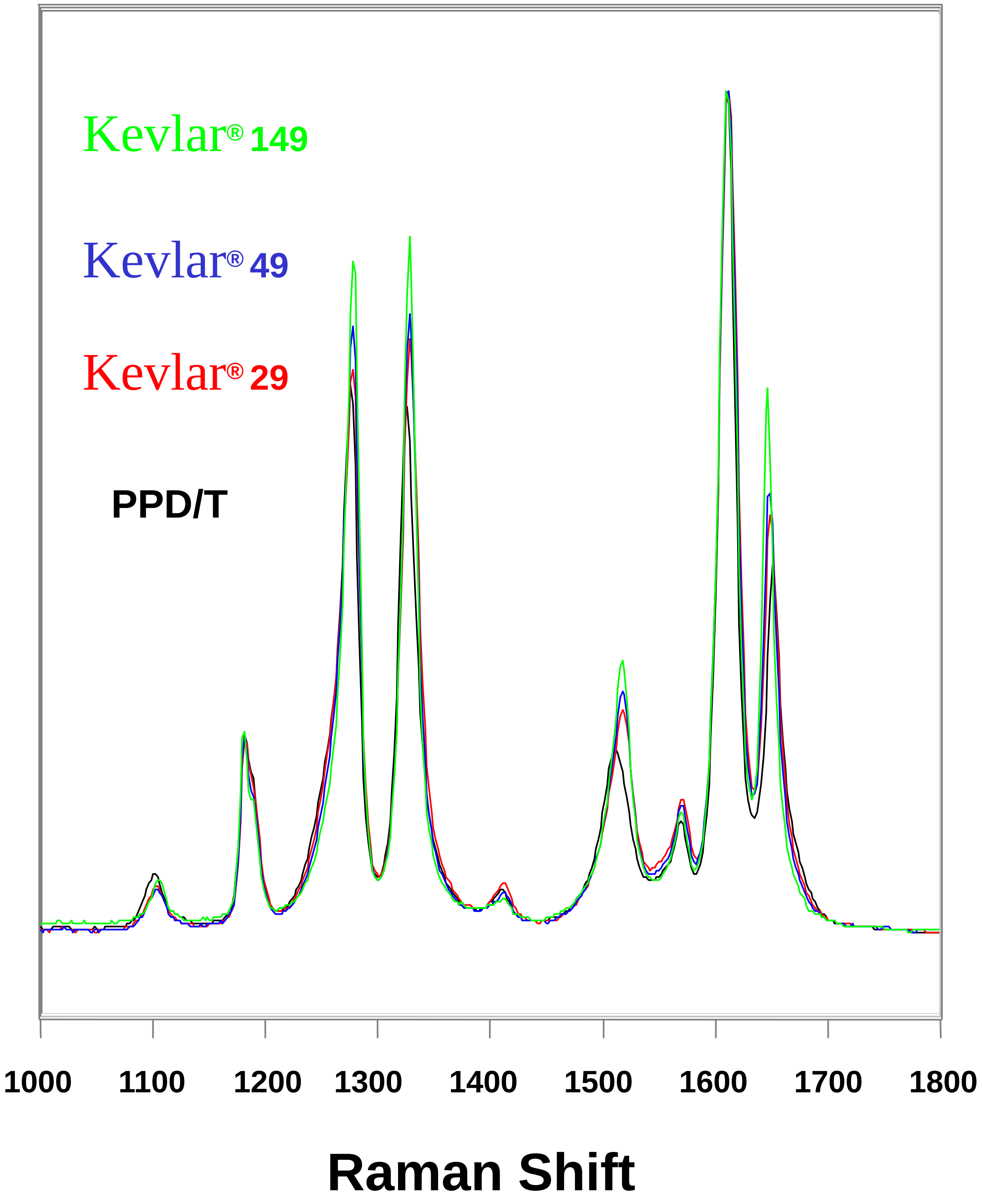
Figure 6.10 “Fundamentals of Polymer Science”

Other examples of crystal field splittings in polyethylene.

Crystallinity

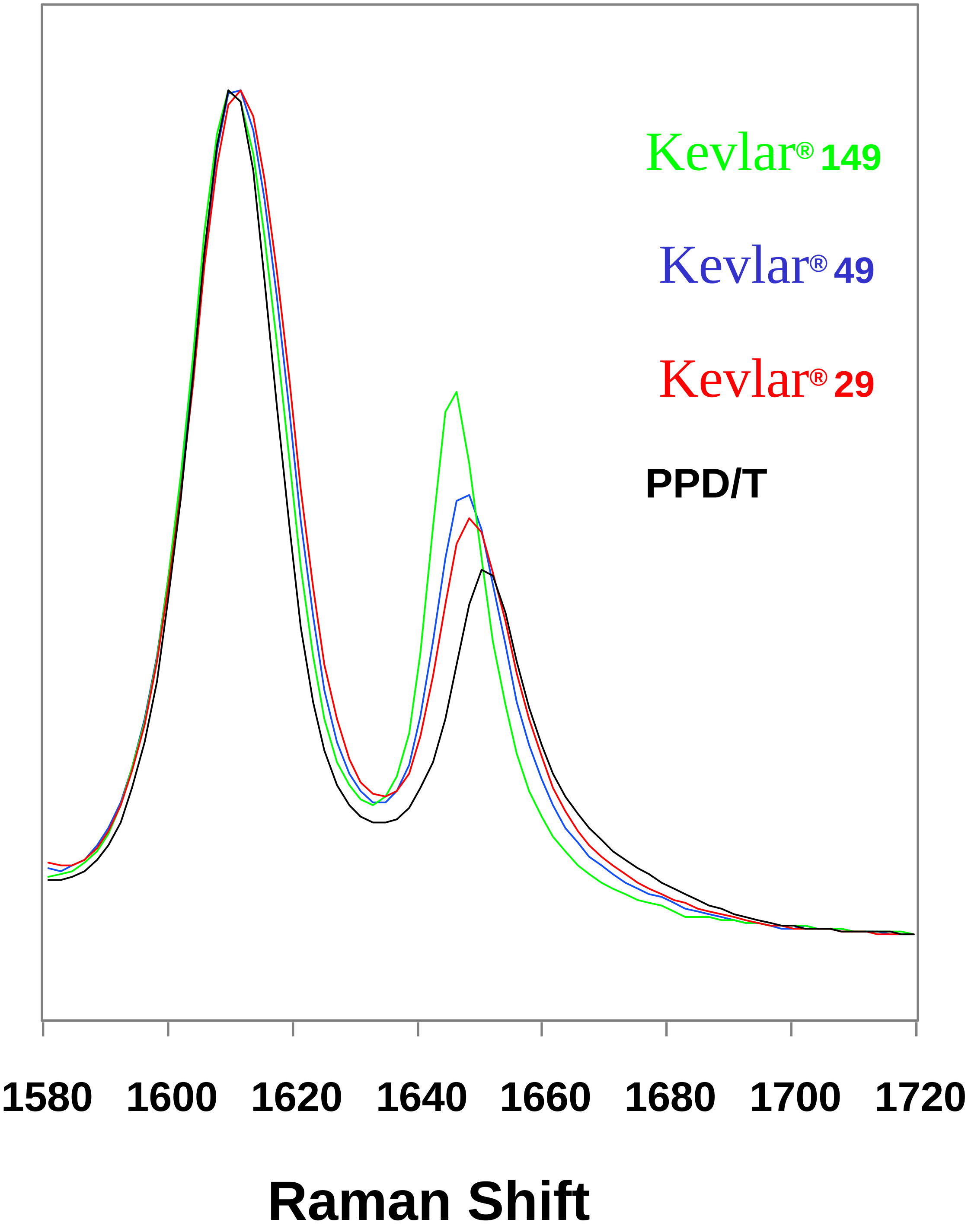
Spectral changes are usually associated with changes in conformational populations and intramolecular interactions NOT intermolecular interactions. Therefore, these are an indirect measure of crystallinity at best!

Kevlar® Fibers and Polymer



One can observe the effects of increasing crystallinity in this system by observing the decrease in frequency and bandwidth of the carbonyl stretch.

Kevlar® Fibers and Polymer

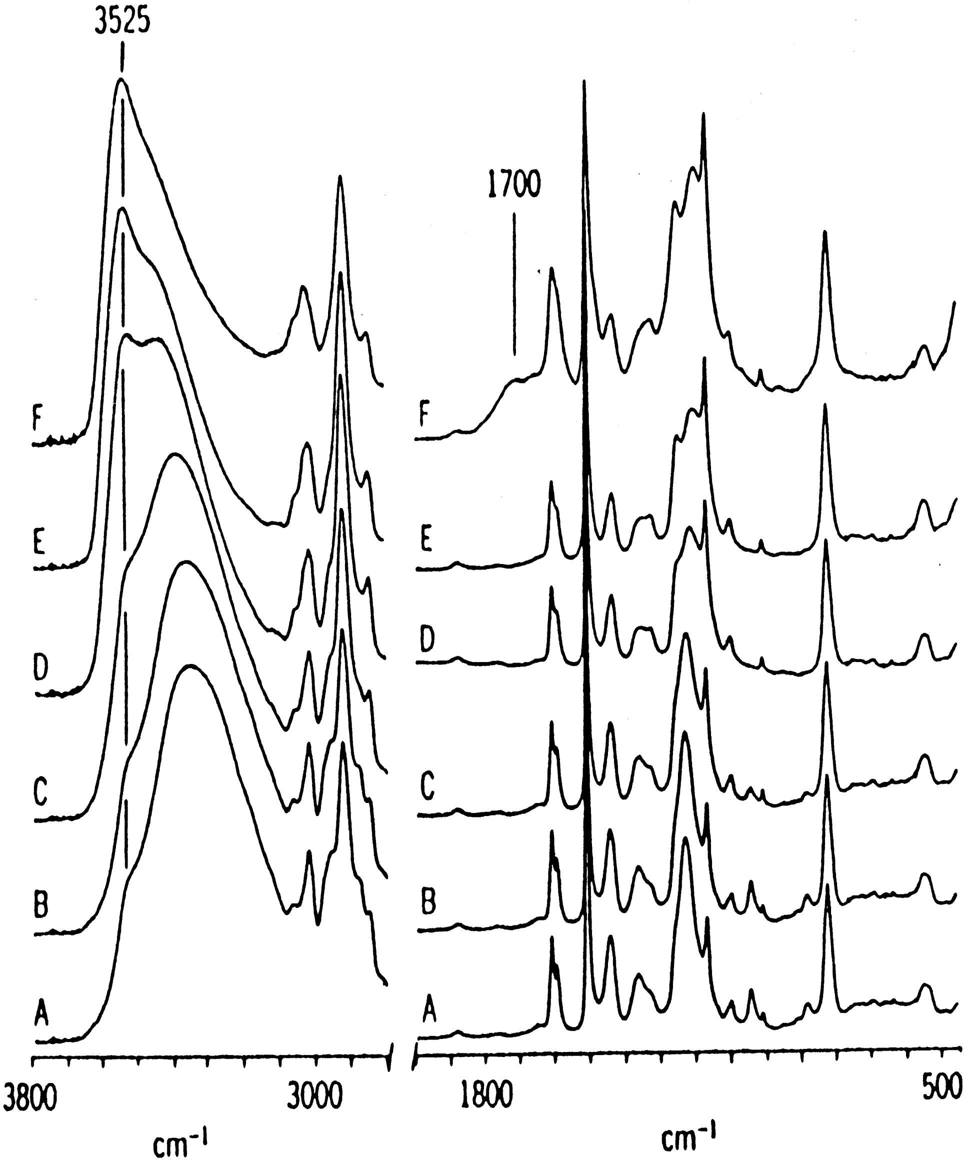


Such a shift to lower energy and decrease in bandwidth can be easily understood by thinking about the perfection of the hydrogen bonded network. As the network becomes more regular(crystalline), the H bonds become on average a little stronger and thus the C=O stretch shifts to lower frequency. Simultaneously, the environment becomes more regular and restricted thus reducing the bandwidth, which is a measure of the distribution of differing environments.

Physical Effects

- Temperature
    - H bonding
    - Conformational populations
    - Crystallinity
- Stress
    - Conformational populations
    - Crystallinity
    - Orientation

An additional aspect of polymer spectroscopy, which contributes to the complexity is the dependence upon external effects like temperature and stress. These can affect conformational state populations and chain orientation, thus distorting the spectra.



(a) (b)

Figure 6.6 The infrared spectrum of atatic poly(4-vinyl phenol) as a function of temperature: (A) 30°C; (B) 50°C; (C) 100°C; (D) 150°C; (E) 200°C and (F) 250°C.

Figure 6.6 “Fundamentals of Polymer Science”

Temperature can have a large effect on vibrational modes which are involved in hydrogen bonding. Heating can change the equilibrium between hydrogen bonded and free O-H species as seen in the 3500 cm^{-1} region. One can also see the effect in the C-O stretching region.

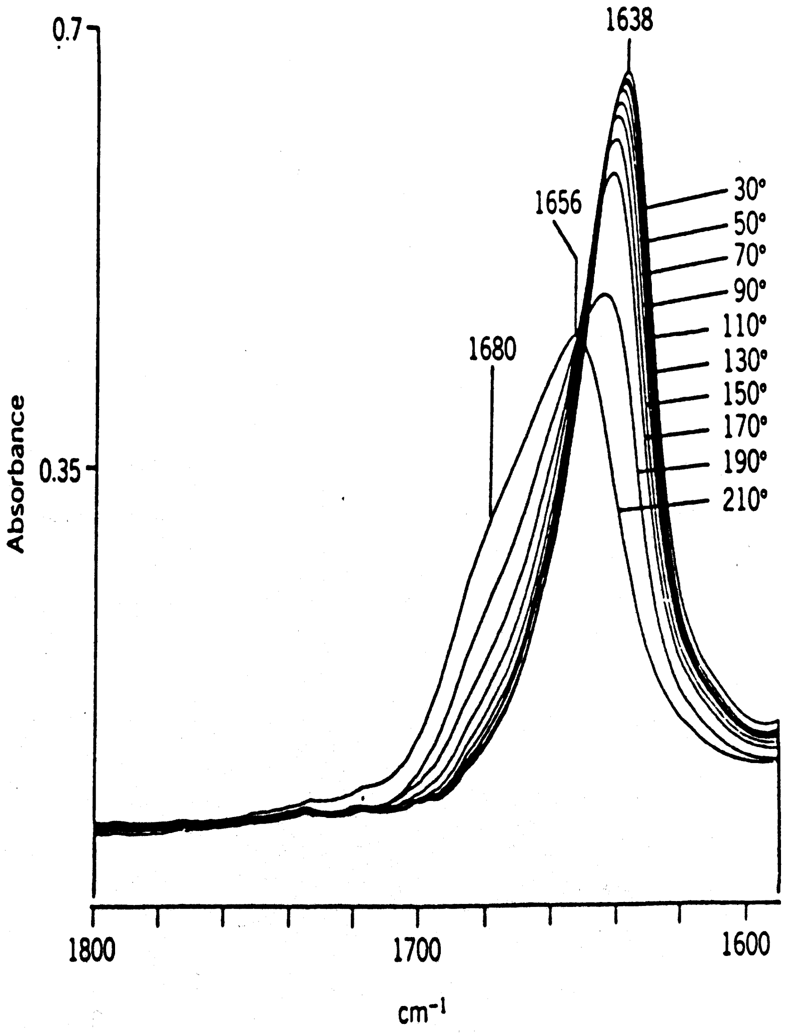


Figure 6.11 The infrared spectrum of nylon 11 in the Amide I region as a function of temperature.

Figure 6.11 “Fundamentals of Polymer Science”

Similar effects can be seen for the C=O stretching mode in nylons. As the degree of H-bonding is reduced at higher temperatures, the C=O average frequency shifts to high values.

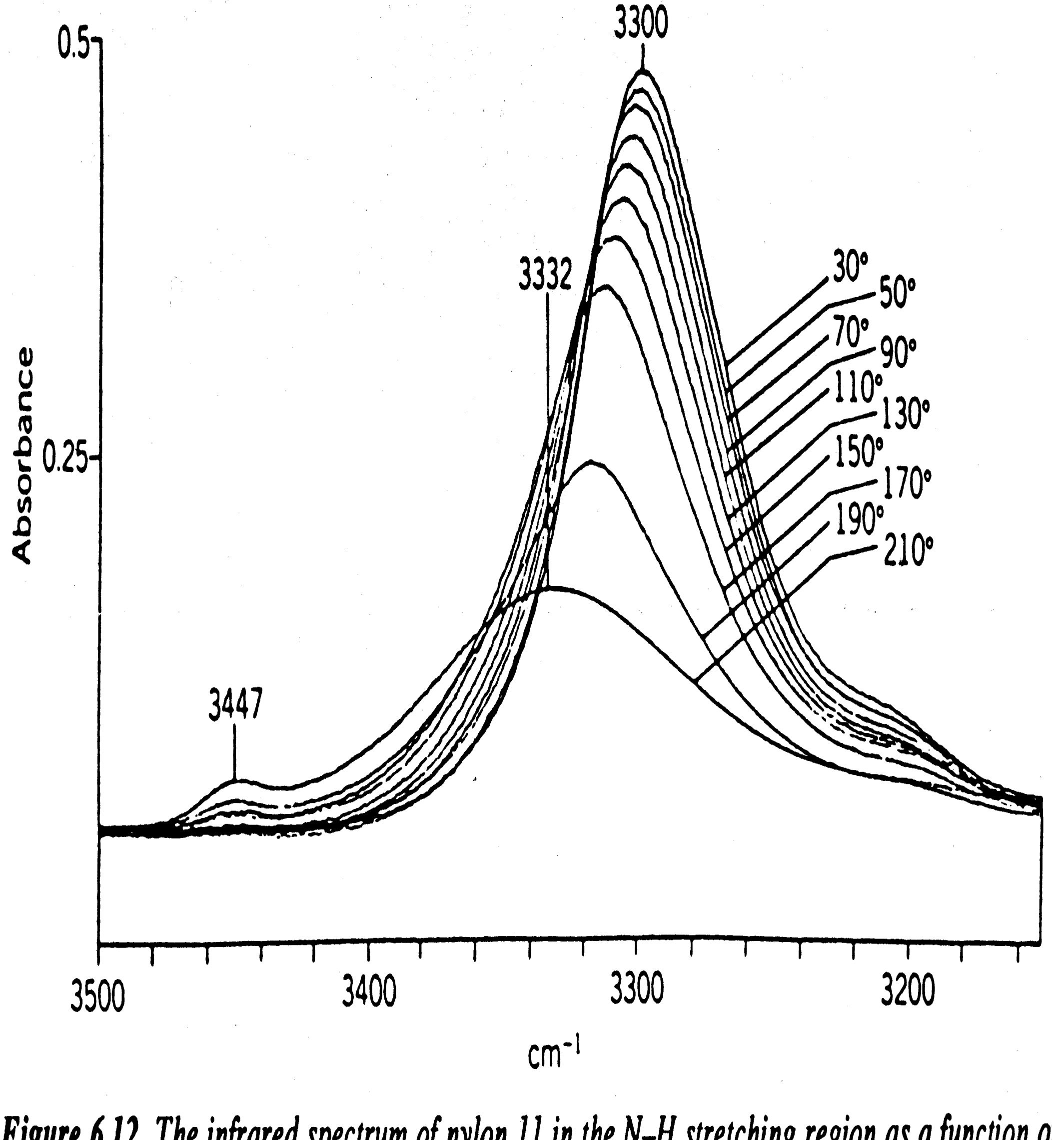


Figure 6.12 The infrared spectrum of nylon 11 in the N–H stretching region as a function of temperature.

Figure 6.12 "Fundamentals of Polymer Science"

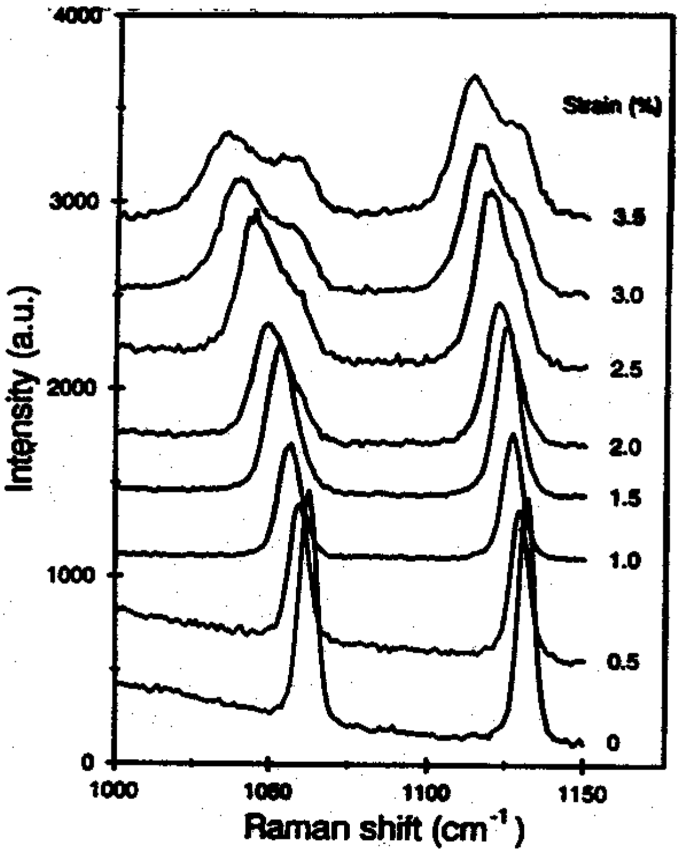


Figure 2. Raman spectra of 149 GPa gel-spun ultra-drawn PE fiber recorded at 240 K after successive strain steps using the Jobin-Yvon HG2S monochromator.

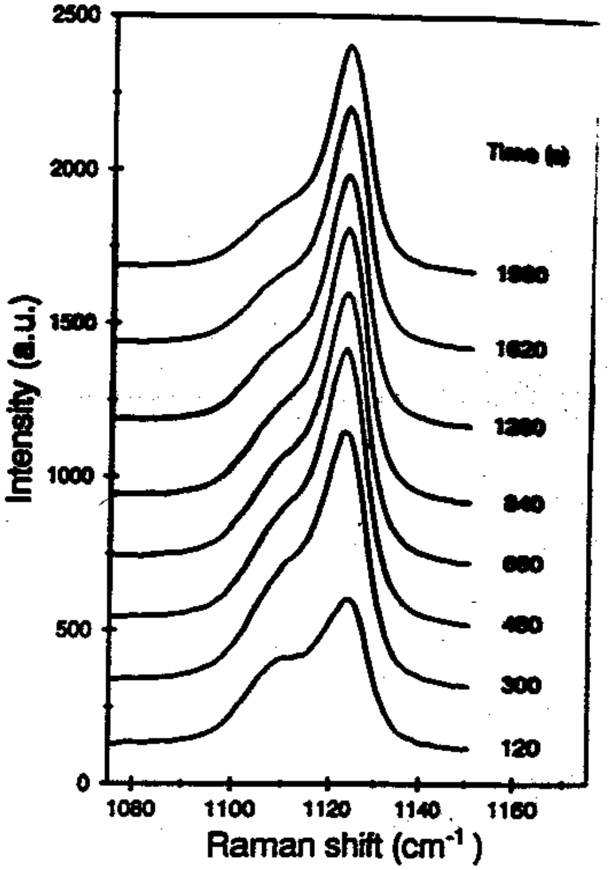


Figure 4. Raman spectra recorded during stress rel ation at 293 K (strain 3.4%).

Moonen, Roovers, Meier, and Kip
J. Poly. Sci. Poly. Phys. 30, 1992 pp 361-372

In a similar fashion, stress applied to polymers can introduce changes in the vibrational spectrum as the chain conformational populations are shifted.

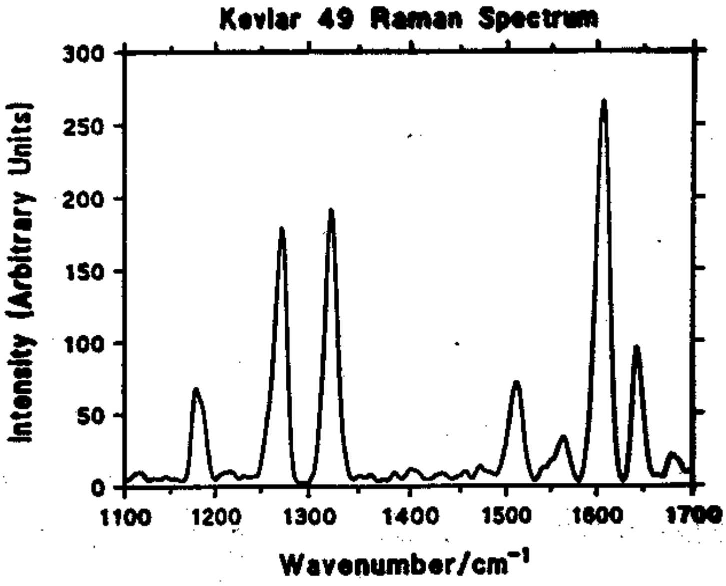


Figure 1. Raman spectrum for a single filament of Kevlar 49 in the region 1100–1700 cm^{-1} obtained using a lower-power He–Ne laser.

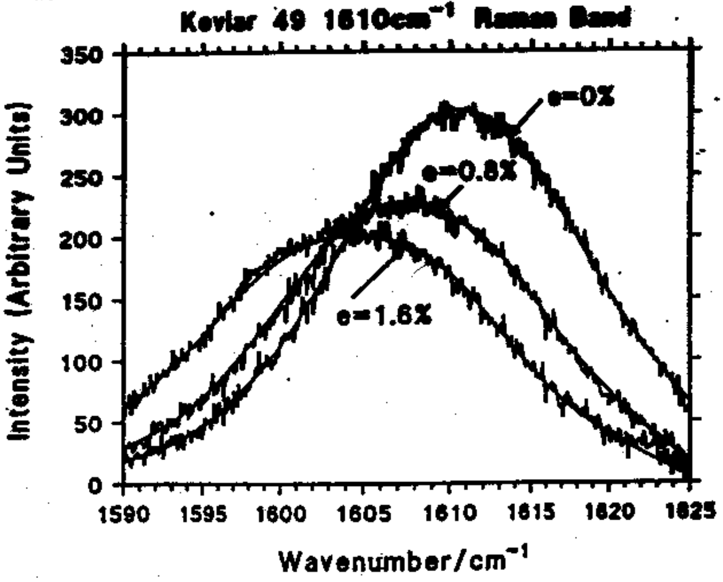


Figure 3. Shift in the position of the 1610 cm^{-1} Raman band for Kevlar 49 at different levels of tensile strain (indicated).

Andrews, and Young
J. Raman Spectrosc. 24, 1993 pp539-544

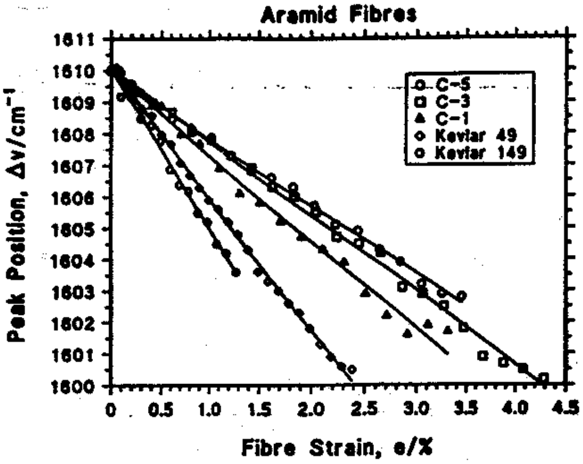


Figure 4. Variation of the peak position of the 1610 cm^{-1} Raman band with tensile fibre strain for the five different aramid fibres. (○) C-5; (□) C-3; (△) C-1; (◇) Kevlar 49; (○) Kevlar 149.

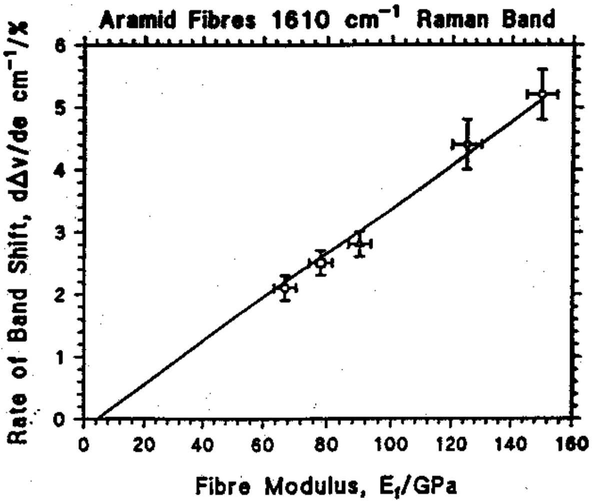


Figure 5. Dependence of the rate of shift per unit strain for the 1610 cm^{-1} Raman band on fibre modulus for the five different aramid fibres shown in Fig. 4. Symbols as in Fig. 4.

Andrews, and Young
J. Raman Spectrosc. 24, 1993 pp539-544

Even when we don't completely understand the mechanism of stress induced frequency shifts, we can make use of them. A plot of frequency shift versus strain is linear and the slope scales with the macroscopic modulus for aramid fibers. This supports our contention that vibrational spectroscopy provides a means of connecting molecular level effects with macroscopic properties.

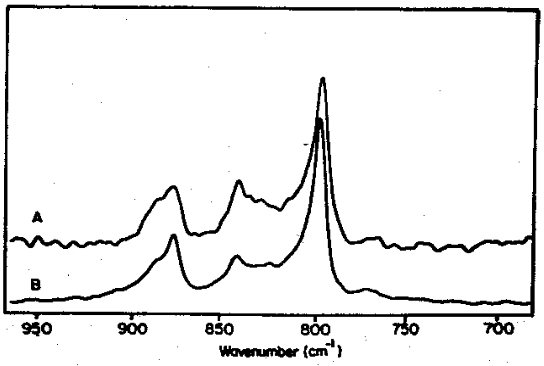


Figure 4 Raman spectra of PVF$_2$ recorded in the centre of the Knoop microindentation (A) and outside the deformed zone (B)

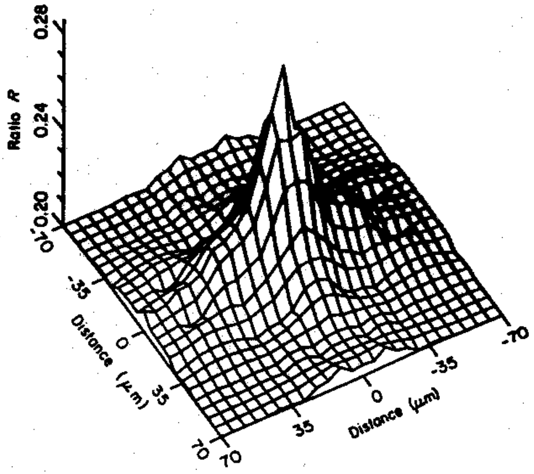


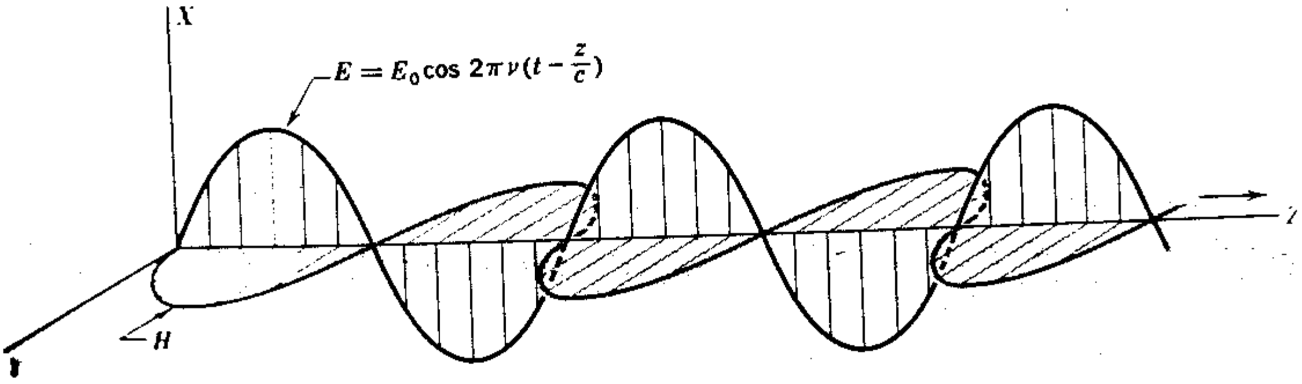
Figure 5 Three-dimensional map showing the variation of the ratio *R* along the Vickers indentation

Jawhari, Merino, Cabello, and Pastor

Polymer 34(8), 1993, pp1613-1619

This shows that the micro Raman spectrum can be used to correlate regions of the stressed sample with stress induced crystallization.

FIG. 1 Plane-polarized electromagnetic radiation.



Oscillating dipoles can couple to the E field (or the H field) but NOT along the propagation direction.

Infrared Dichroism

$$I = C*(\boldsymbol{E}\cdot \boldsymbol{M})^2 = C*(E*M*\cos(\Theta))^2$$

where C = constant

$\boldsymbol{E}$ = Electric Field Moment

$\boldsymbol{M}$ = Molecular Transition Moment

E = magnitude of $\boldsymbol{E}$

M = magnitude of $\boldsymbol{M}$

Θ = angle between $\boldsymbol{E}$ and $\boldsymbol{M}$

$\boldsymbol{M}$ has both direction and magnitude

Note: Once the axis system has been defined we have:

$$I_{||} \;\alpha\; \cos^2(\Theta)$$

$$I_{\perp} \;\alpha\; \sin^2(\Theta)$$

The infrared orientational information is contained in a dot product. We only care about the orientation of the incident E field and the orientation of the dipole moment vector associated with the vibration.

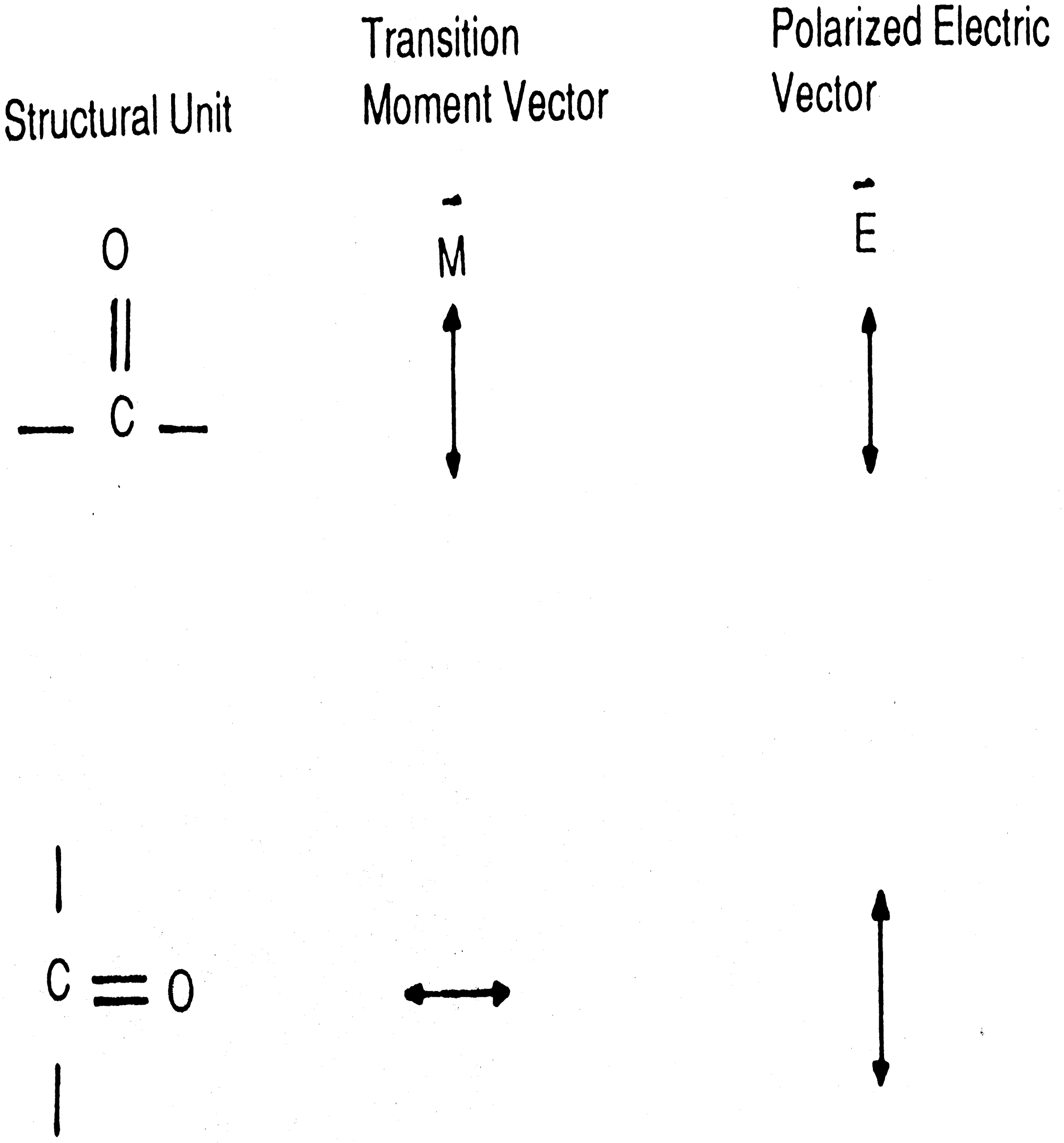


Figure 2.7. Linearly polarized IR absorbance of structural units.

For a simple vibration like a C=O stretch it is easy to visualize. The maximum absorption will occur when the E field is aligned with the C=O axis.

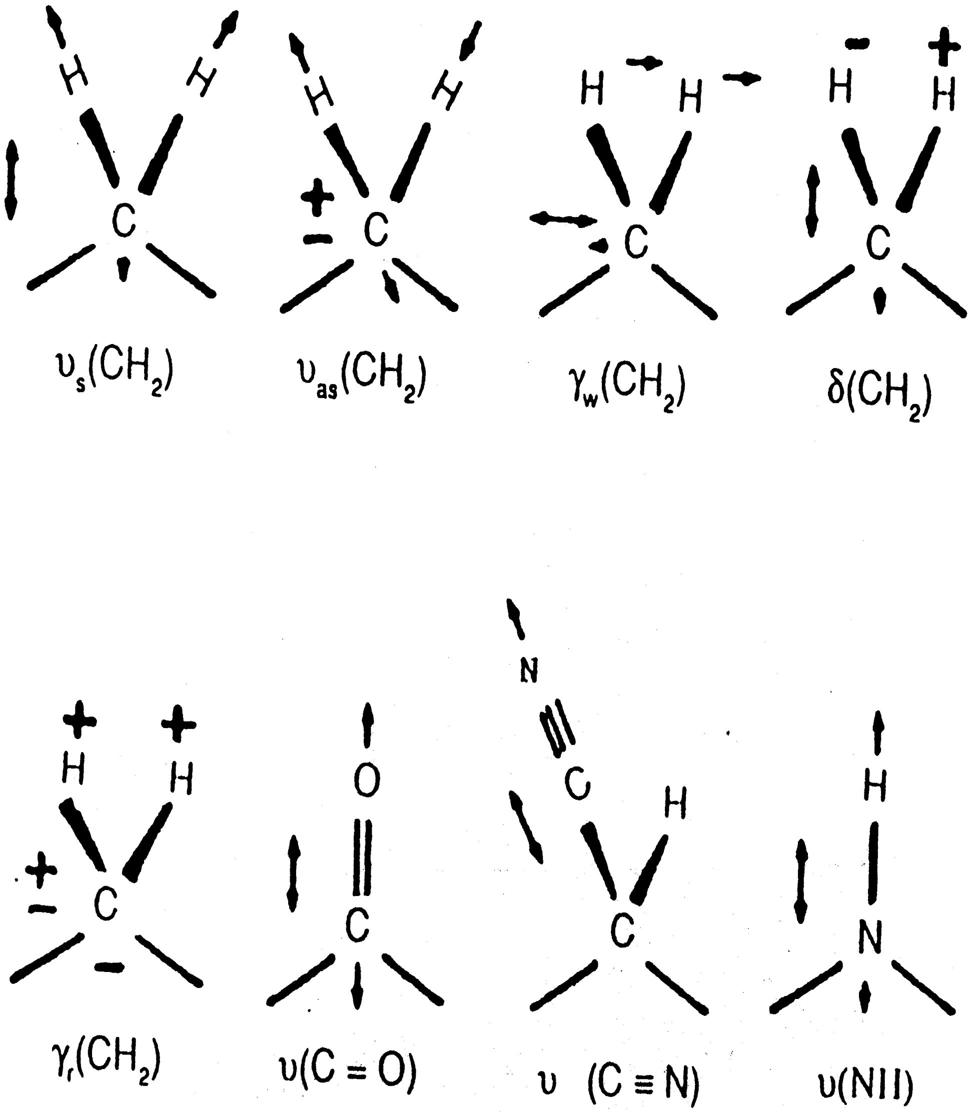
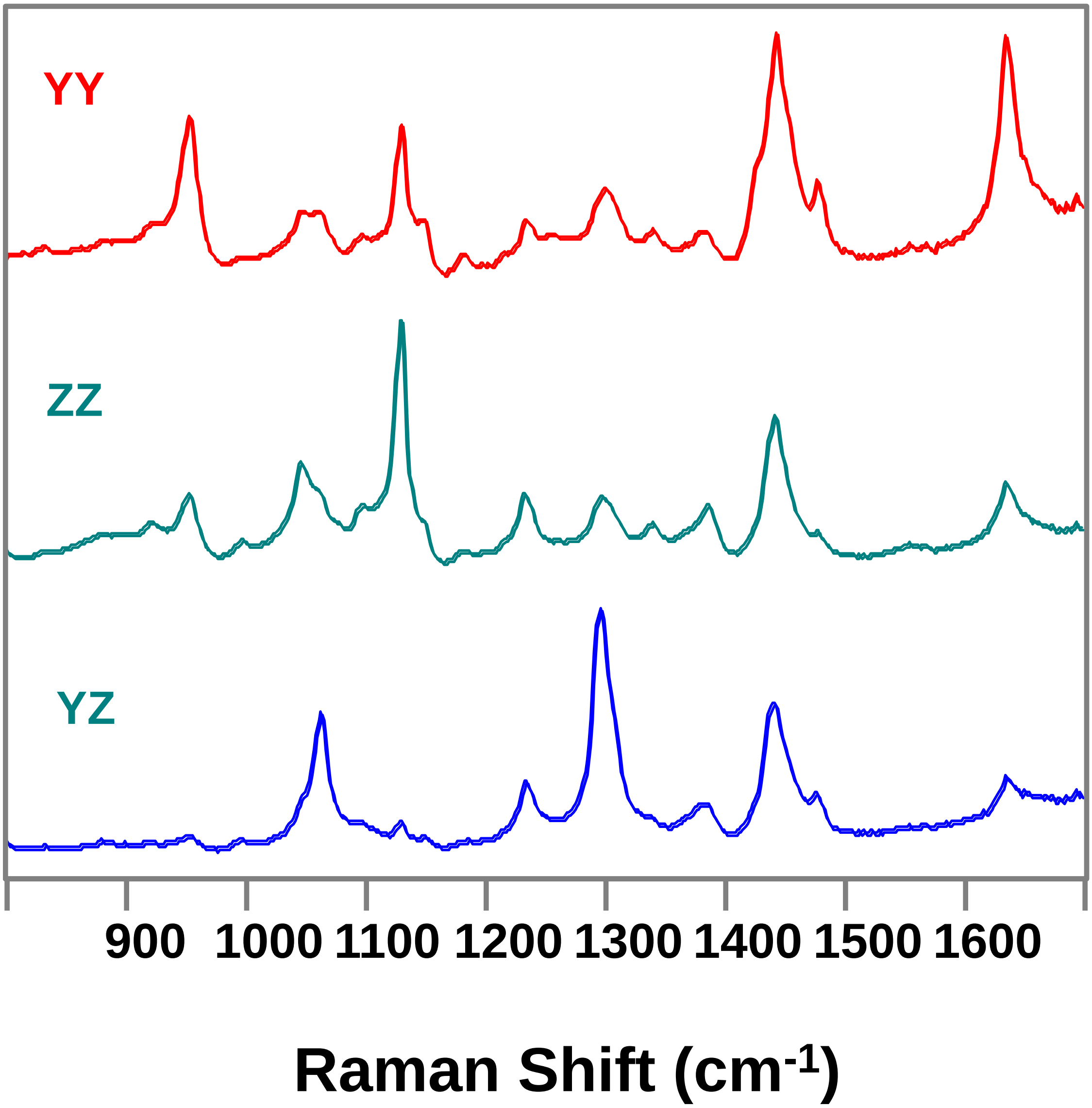


Figure 2.6. The transition-moment directions of some vibrational modes. (Reproduced with permission from reference 15. Copyright 1980 Marcel Dekker, Inc.)

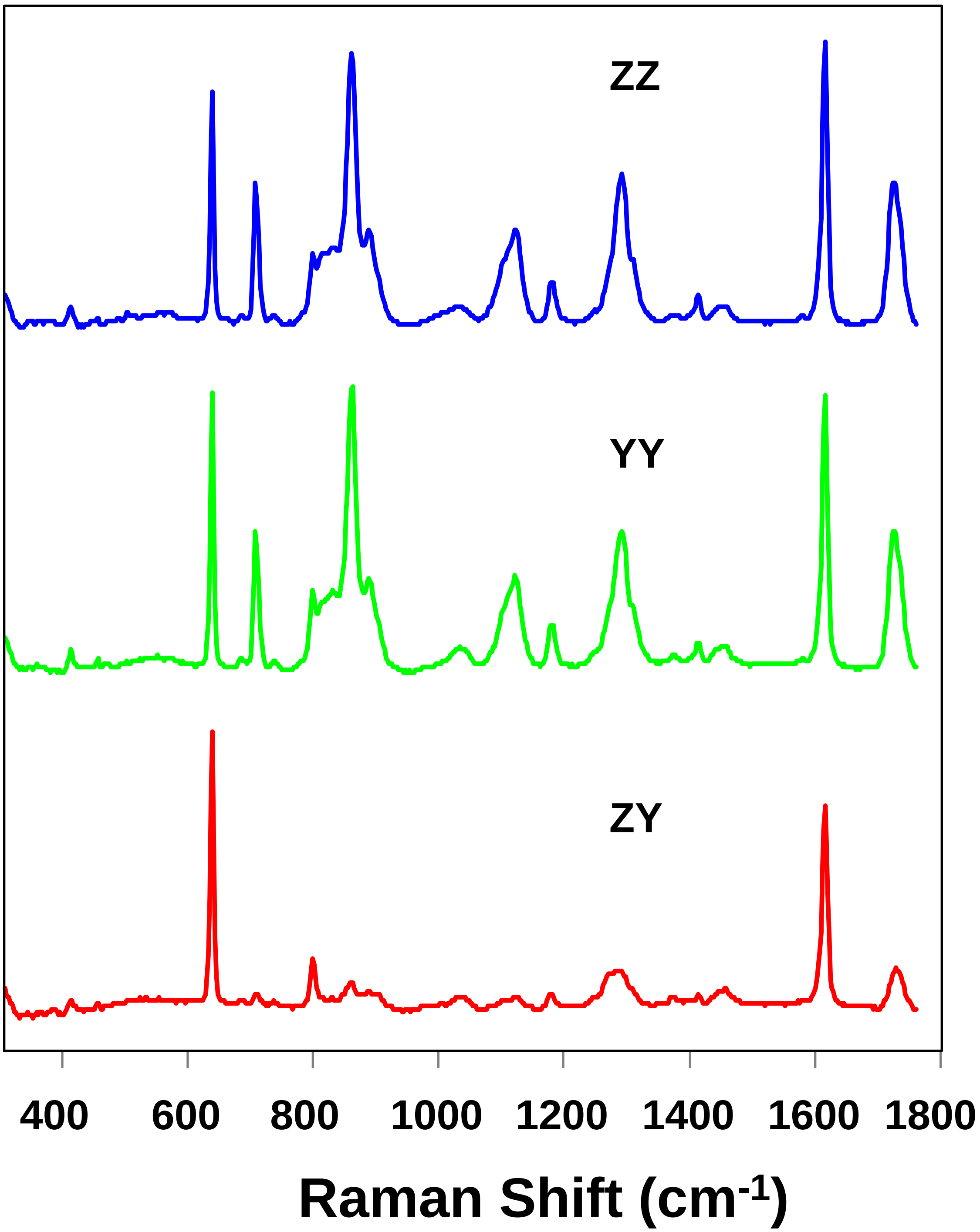
There are other common vibrational modes where it is trivial to estimate the direction of the dipole moment vector during the vibration. For both the symmetric and antisymmetric stretches of the CH2 group, the dipole moment vector is perpendicular to the chain axis (for a zig-zag methylene chain).

Nylon 66 fibers
Polarized Raman scattering



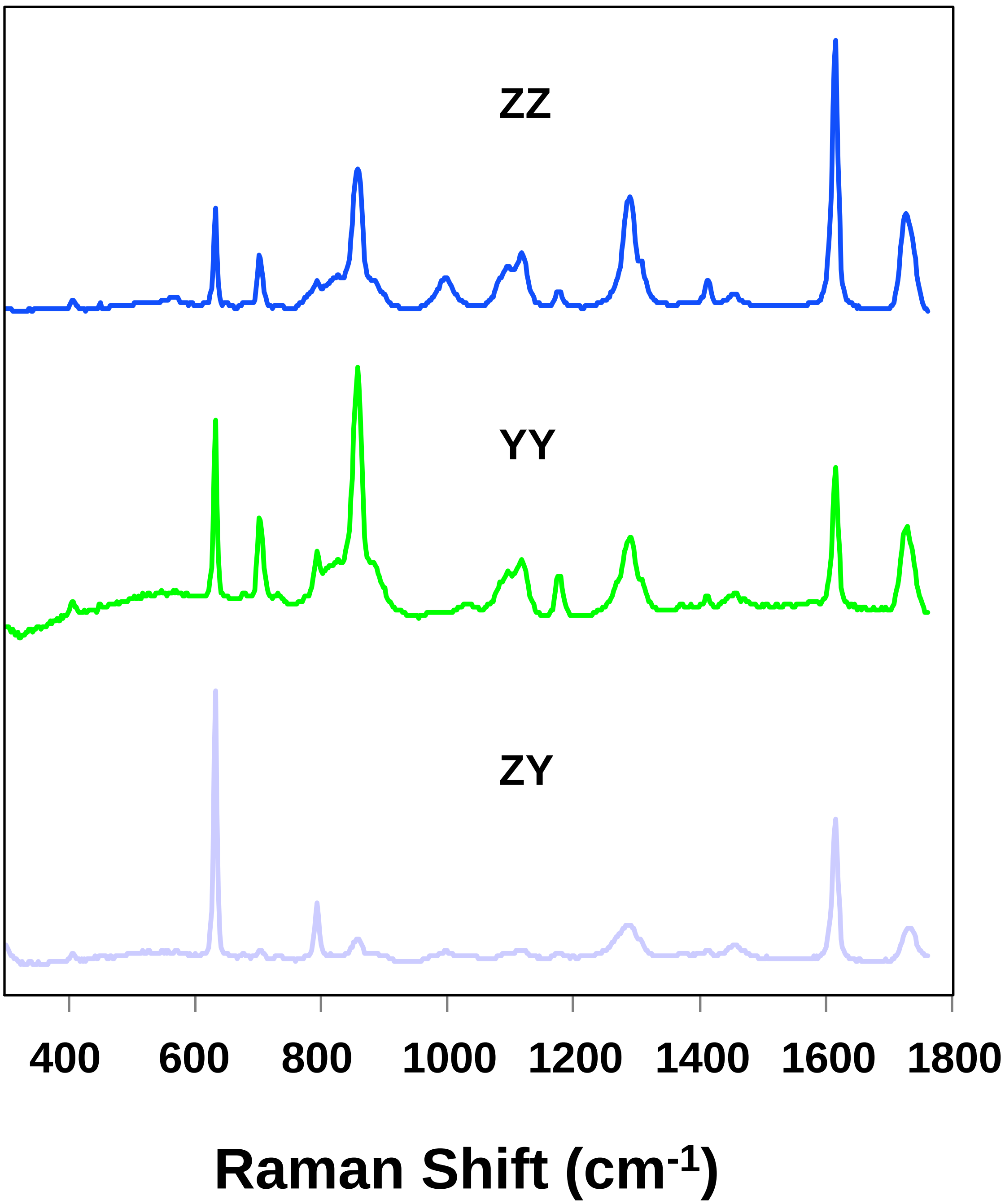
For nylon fibers which are drawn in the spinning process it is clear that there is orientation. One can look at the ratio of the carbonyl stretch to the ring mode at 1600 cm^{-1} and see that the ratio is different for ZZ and YY polarizations.

PET undrawn



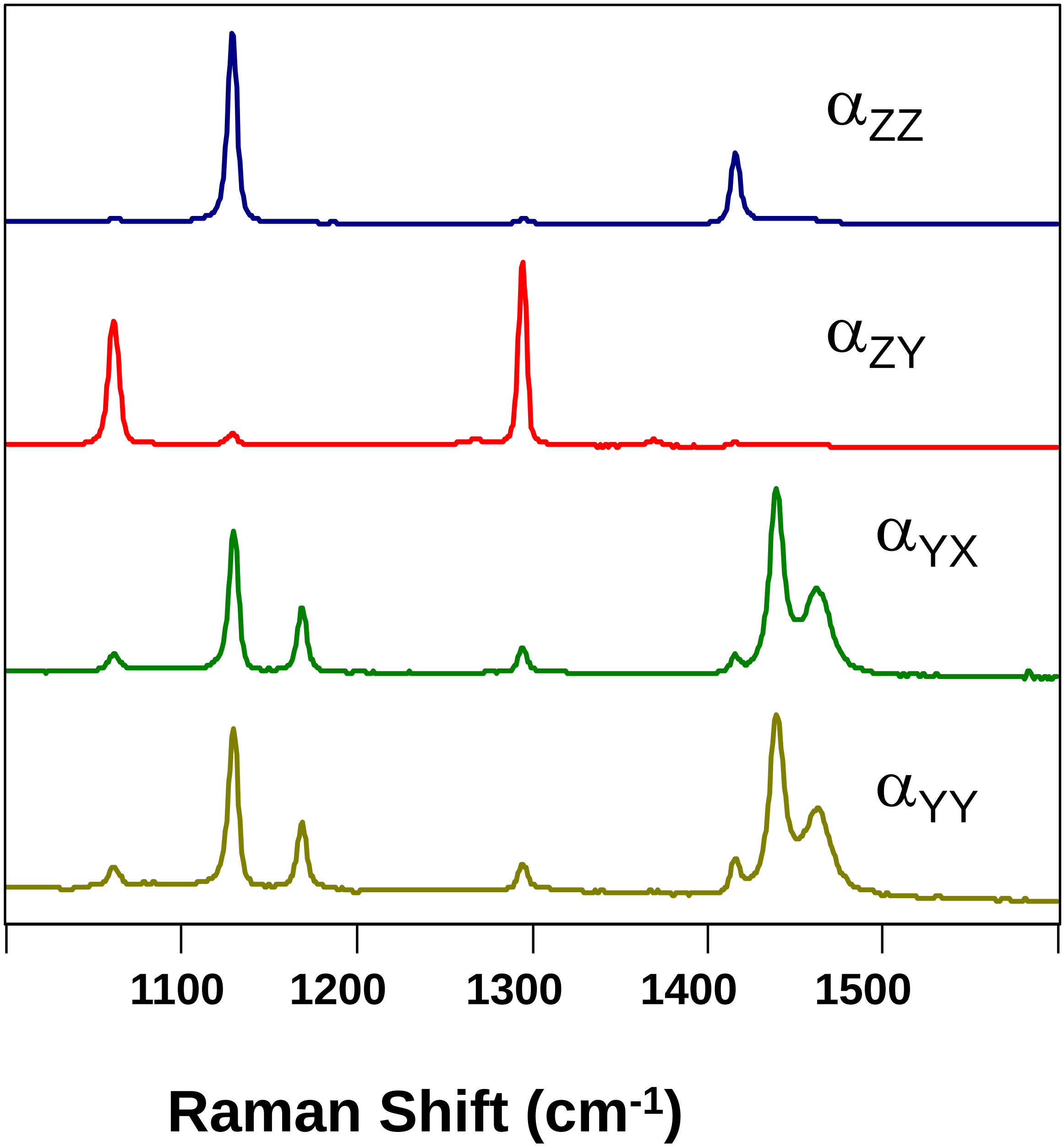
PET fibers can be spun without draw. The absence of draw (other than found in the spin line itself) might be expected to result in minimal orientation. A comparison of ZZ and YY intensities would support this hypothesis. There appears to be little if any orientation for these fibers.

PET drawn



However, when those same fibers are drawn, now there is clear evidence of orientation.

Polyethylene Fibers



These are four of the five independent intensities which we need to calculate P2 and P4.

Infrared & Raman Users Group

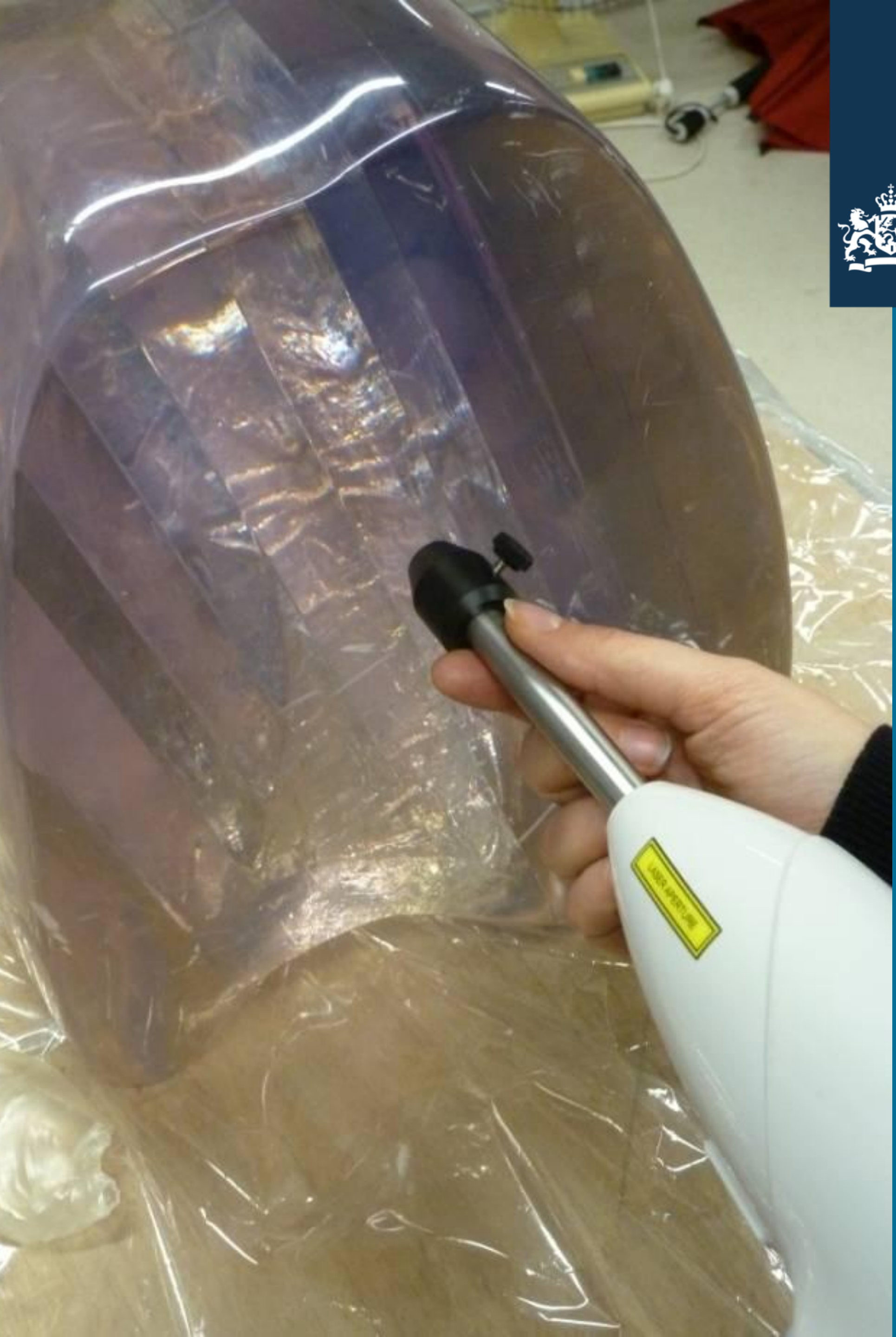
Raman Spectroscopy Workshop

The identification of plastics in modern & contemporary art objects using fibre optic Raman

Suzan de Groot

Cultural Heritage Agency of the Netherlands, Amsterdam, NL

FRIDAY, SEPTEMBER 28: LECTURE 5



Rijksdienst voor het Cultureel Erfgoed
Ministerie van Onderwijs, Cultuur en Wetenschap

The identification of plastics in modern and contemporary art objects using Fibre Optics Raman Spectroscopy

Suzan de Groot
Thea van Oosten
Baudien te Nijenhuis

Outline

- POPART
- SamCo
- Challenges
- Round Robin test
- Identifying plastics in design objects
- Identifying plastics in museum objects
- Identifying plastics in museum objects on site

Which plastics are in my collection?

Why identify plastics?

- understanding degradation
- estimating risk
- defining appropriate conservation treatments

How to identify plastics?

- suitable analytical techniques
- support of reference materials

Plastics in collections

Acetal Resin	POM
Acrylic	PMMA
Acrylonitrile-butadiene-styrene	ABS
Styrene Butadiene Rubber	SBR
Polystyrene	PS
Styrene Acrylonitrile	SAN
Cellophane	CE
Cellulose Acetate	CA
Cellulose Acetate Propionate	CAP
Cellulose Nitrate	CN
Epoxy	EP
Ethylene Vinyl Acetate	EVA
Glass fibre reinforced polyester	GRP
Nylon/Polyamide (Type 6)	PA
Nylon/Polyamide (Type 6,6)	PA
Phenol Formaldehyde	PF
Melamine Formaldehyde	MF
Urea Formaldehyde	UF

Polycarbonate	PC
Polybutylene terephthalate	PBT
Polyetylene terephthalate	PET
Polyether-etherketone	PEEK
Polyethylene	PE
Polypropylene	PP
Polytetrafluoroethylene	PTFE
Polyurethane flexible foam (ester + ether)	PUR
Urethane Elastomer Thermoplastic	TPU
Polyvinylidene Fluoride	PVDF
Polyvinylidene Chloride	PVDC
Silicone rubber	SI

Sample Collection (SamCo)

SamCo:
a well characterized reference sample collection representing new and degraded plastics found in museum collections

Objectives:
- evaluate suitable analytical tools for the identification of plastics
- support these analyses with a library of reference spectra

SamCo Team:
Cultural Heritage Agency of the Netherlands (RCE)
Victoria and Albert Museum (V&A)
National Museum of Denmark (Natmus)

POPART
Preservation Of Plastic ARTefacts in museum collections

SEVENTH FRAMEWORK PROGRAMME

SamCo – Selection criteria

- 46 types of plastics (natural, semi-synthetic and synthetic)

- Two types of reference for each type of plastics: reference standards and reference objects

Reference STANDARDS:

↓

Polymethylmethacrylate (Perspex)

Reference OBJECTS :

↓

Polymethylmethacrylate

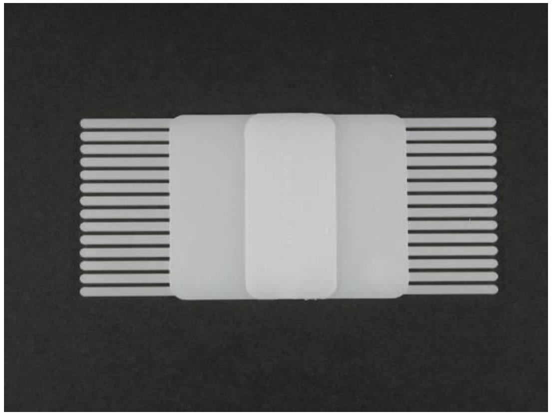
Collecting reference standards

THE ResinKit

A Complete Guide for Identifying and Testing Plastic Resins

- ✓ ResinKit^{TM}

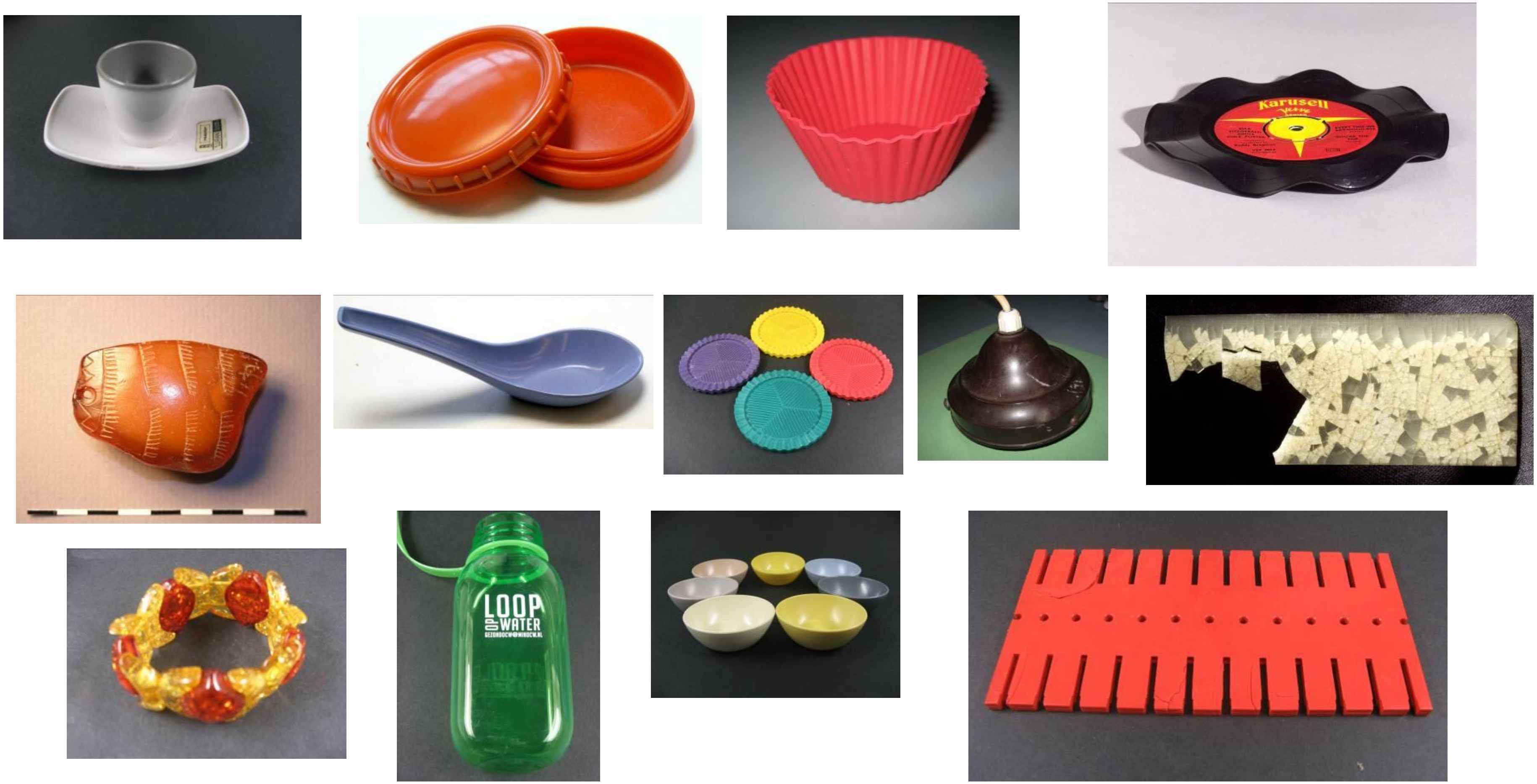
provides samples and complete technical information of the most commonly used thermoplastics resins



Polyethylene high density Resin Kit^{TM}sample

Collecting reference objects

- ✓ RCE –NATMUS-V&A collections and private collections



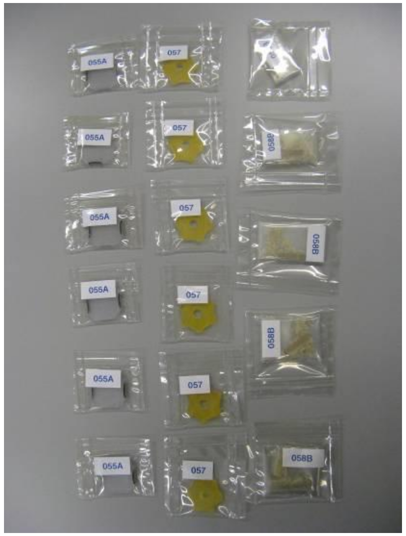
Final selection of SamCo (100 references)

Brenda Keneghan, Thea van Oosten

Cut

Samco references materials placed in 7 boxes one for each partner

Anna Laganà, Yvonne Shashoua



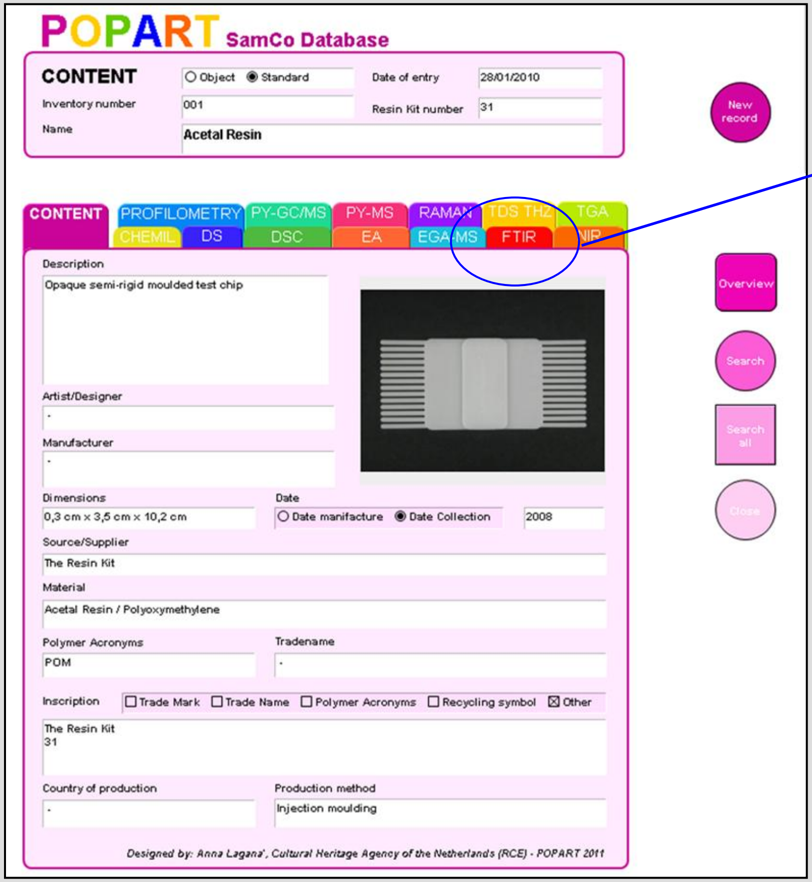
Encapsulation

SamCo

Reference **STANDARDS**

Reference **OBJECTS**

SamCo Database

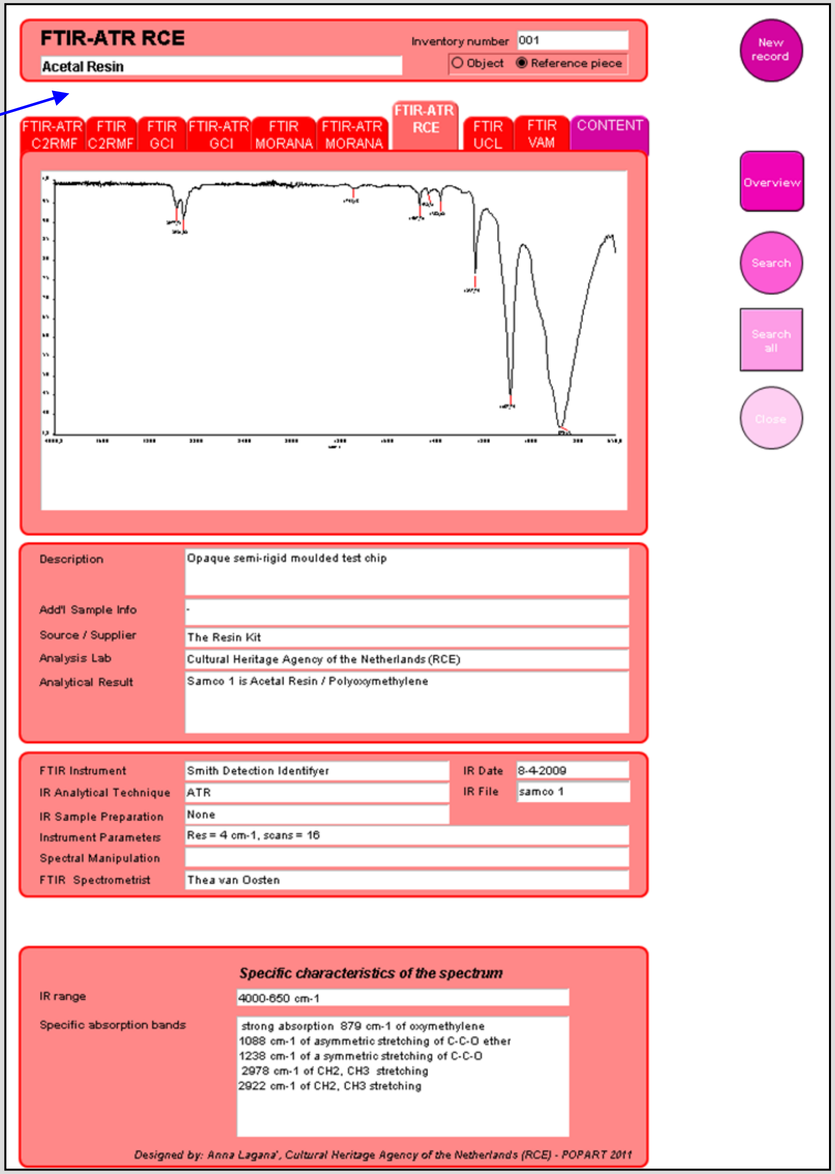


CONTENT

○ Object ● Standard

Date of entry	28/01/2010
Inventory number	001
Resin Kit number	31
Name	**Acetal Resin**
Description	Opaque semi-rigid moulded test chip
Artist/Designer	-
Manufacturer	-
Dimensions	0,3 cm x 3,5 cm x 10,2 cm
Date	○ Date manifacture ● Date Collection 2008
Source/Supplier	The Resin Kit
Material	Acetal Resin / Polyoxymethylene
Polymer Acronyms	POM
Tradename	-
Inscription	☐ Trade Mark ☐ Trade Name ☐ Polymer Acronyms ☐ Recycling symbol ☒ Other
	The Resin Kit 31
Country of production	-
Production method	Injection moulding

Designed by: Anna Lagana', Cultural Heritage Agency of the Netherlands (RCE) - POPART 2011



FTIR-ATR RCE

Inventory number	001
	Acetal Resin
	○ Object ● Reference piece

Description	Opaque semi-rigid moulded test chip
Add'l Sample Info	-
Source / Supplier	The Resin Kit
Analysis Lab	Cultural Heritage Agency of the Netherlands (RCE)
Analytical Result	Samco 1 is Acetal Resin / Polyoxymethylene

FTIR Instrument	Smith Detection Identifyer
IR Date	8-4-2009
IR Analytical Technique	ATR
IR File	samco 1
IR Sample Preparation	None
Instrument Parameters	Res = 4 cm-1, scans = 16
Spectral Manipulation	
FTIR Spectrometrist	Thea van Oosten

Specific characteristics of the spectrum

IR range	4000-650 cm-1
Specific absorption bands	strong absorption 879 cm-1 of oxymethylene 1088 cm-1 of asymmetric stretching of C-C-O ether 1238 cm-1 of a symmetric stretching of C-C-O 2978 cm-1 of CH2, CH3 stretching 2922 cm-1 of CH2, CH3 stretching

Designed by: Anna Lagana', Cultural Heritage Agency of the Netherlands (RCE) - POPART 2011

Identification techniques

Technique	**Fillers (>3%)**	**Plasticizers (> 3 %)**	**invasive sample size**	**noninvasive (fibre optics)**	**Portable**
FTIR	yes	yes	yes 0,1-1 mm^2	yes (no fibre optics)	yes
Raman	yes	yes	yes 0,1-1 mm^2	yes	yes
NIR	no	yes	-	yes	yes
Py-GCMS	no	yes	yes 0,1 mm^2	no	no

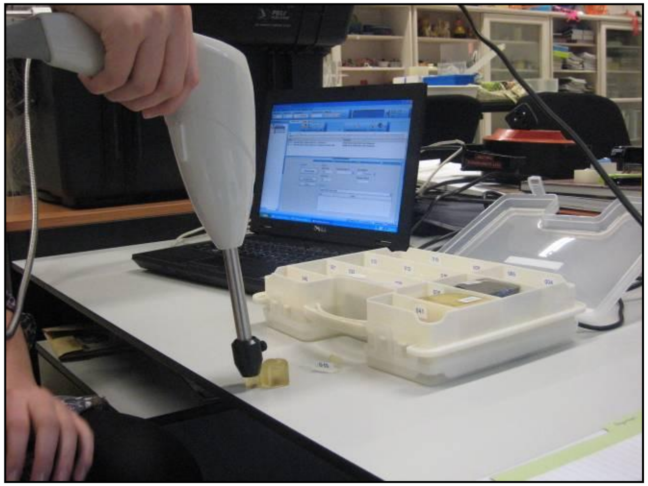
Raman (785 nm)

PerkinElmer Raman
Spectrograph 400F

PerkinElmer Raman
Triggered Fibre Optic Probe

PerkinElmer
Identicheck

Database of SamCo reference spectra



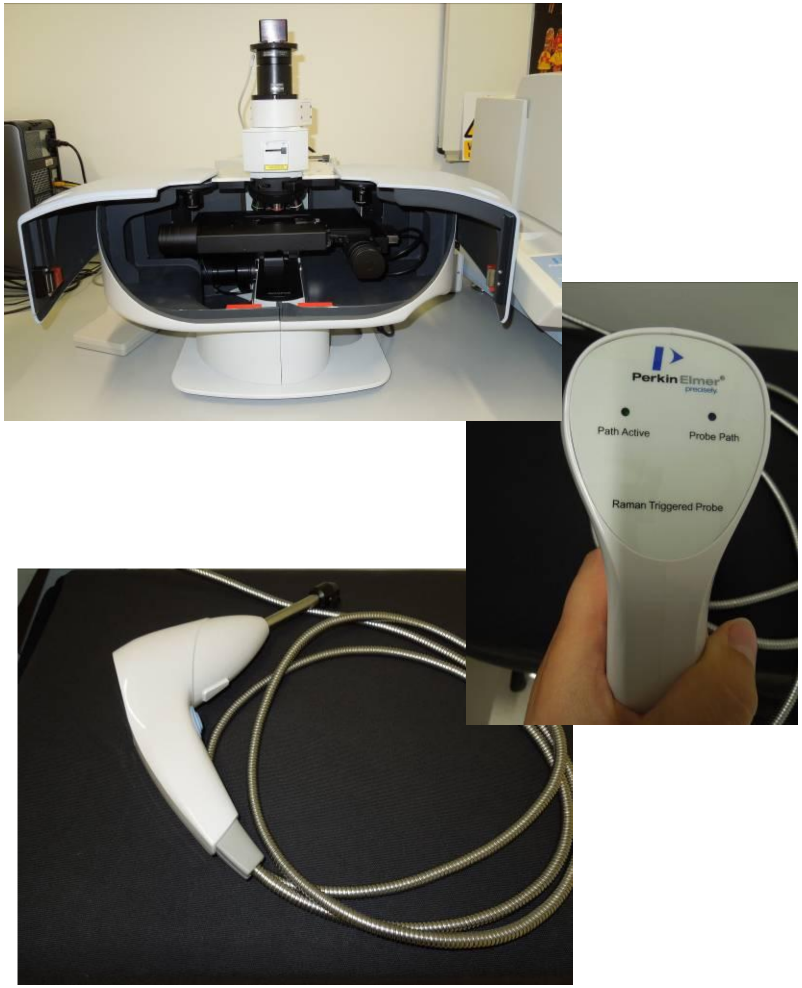
Parameters

Microscope:

Objective: 50X
Spot size: 20 µm
exposure time: avg. 10 sec.
no. of exposures: 50-60
laser power:20-70 mW

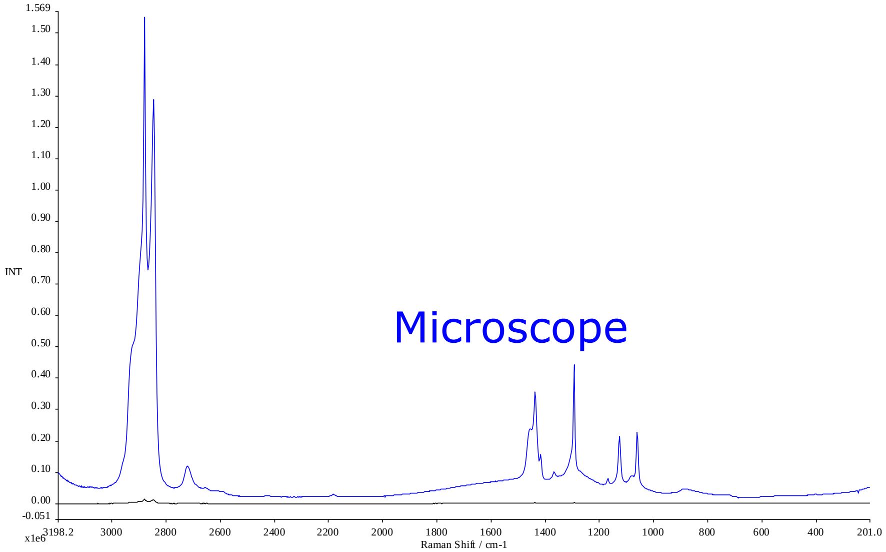
Fibre:

Spot size: 2 mm
Measuring distance: 7 mm
exposure time: 2s
no. of exposures: 2
laser power:20-50 mW



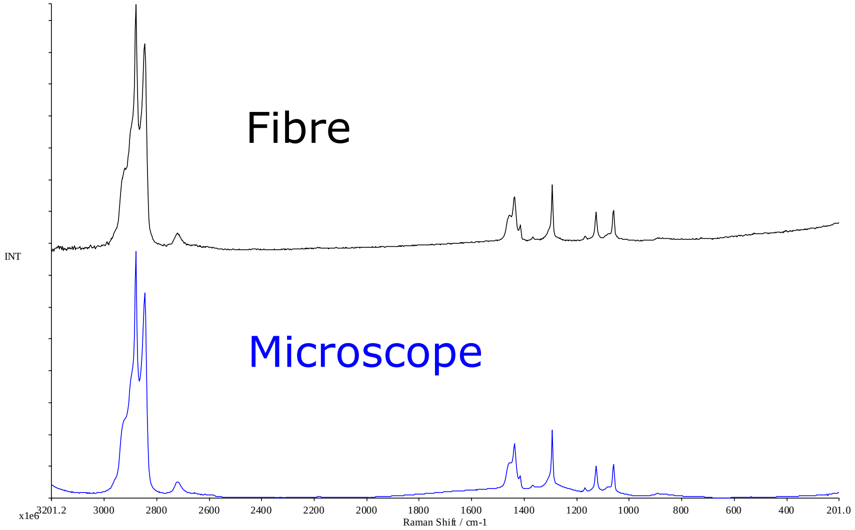
Microscope vs. Fibre

LDPE



Microscope

Fibre



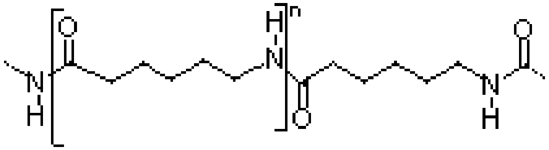
Fibre

Microscope

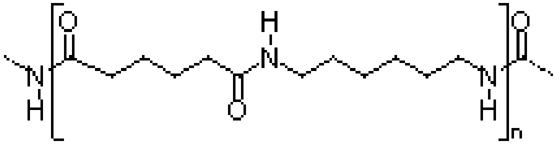
Difference Nylon 6 –Nylon 6,6

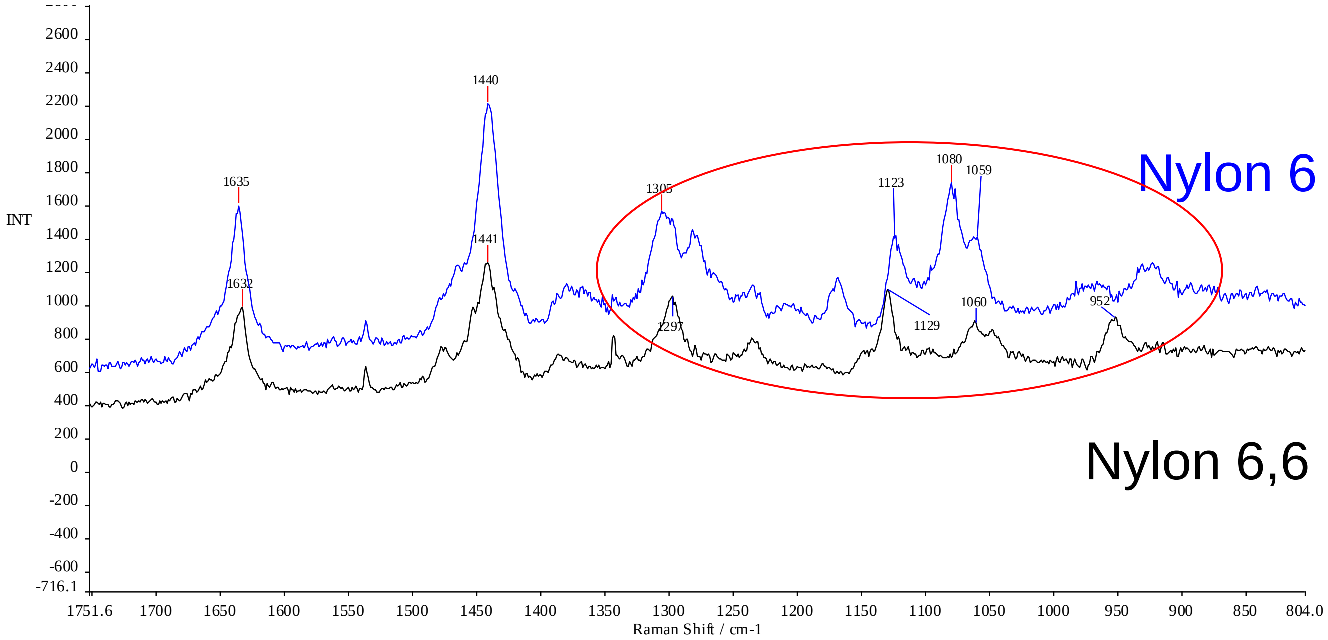
Ernesto Neto,Celula Nave, Boijmans van Beuningen Museum

Nylon 6

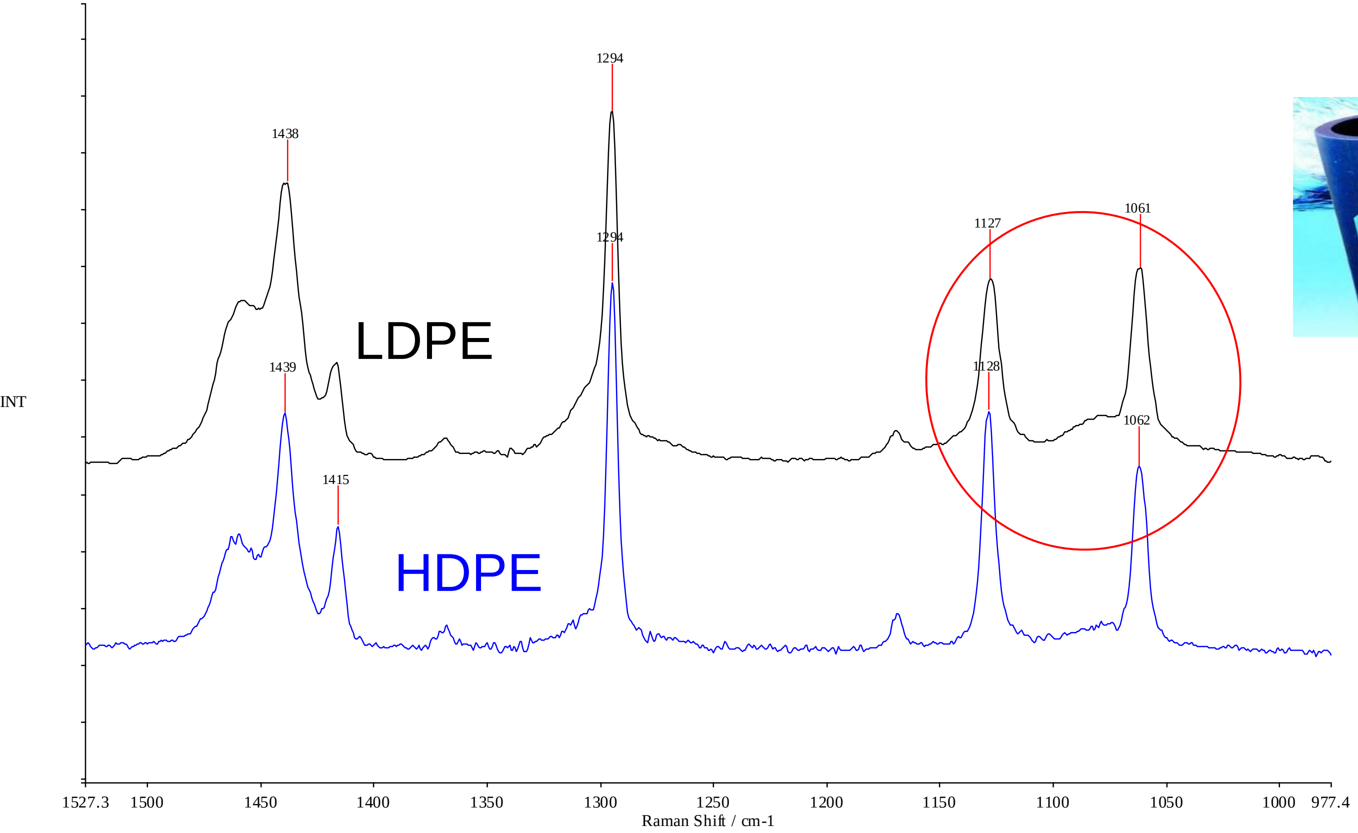


Nylon 6,6

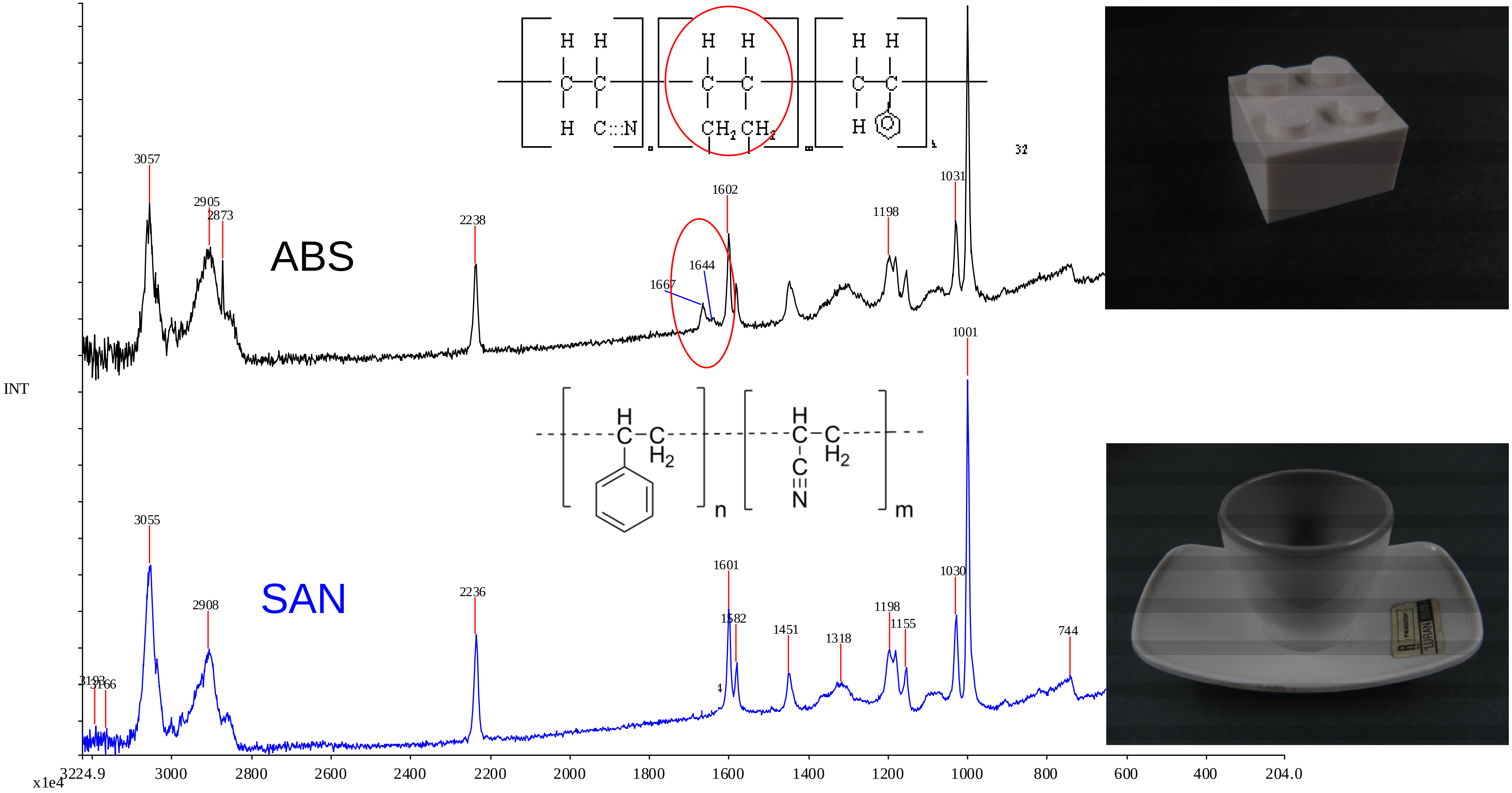




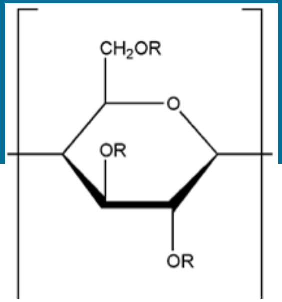
Difference HDPE-LDPE

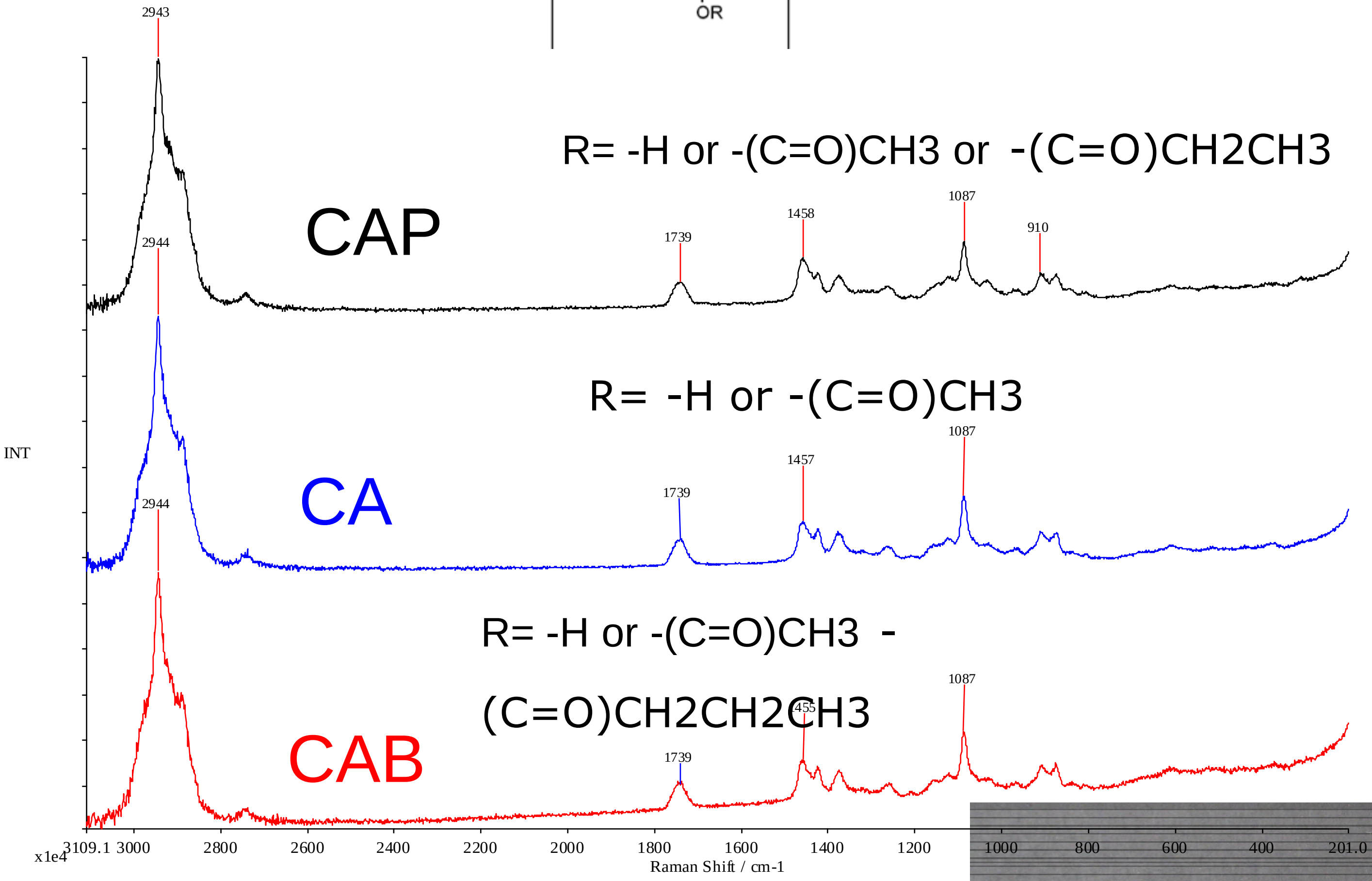


Difference ABS-SAN



Cellulose esters





CAP

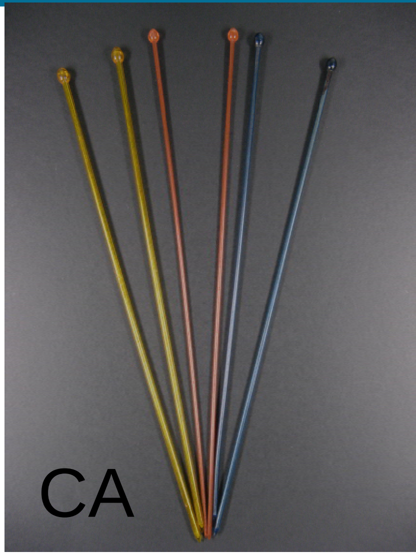
R= -H or -(C=O)CH3 or -(C=O)CH2CH3

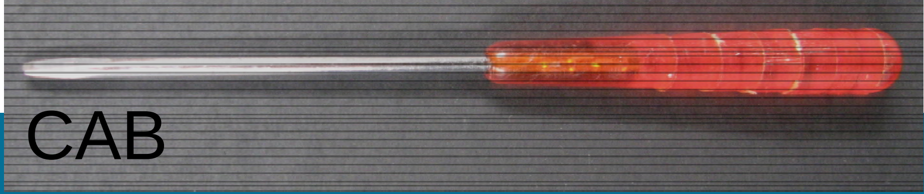
CA

R= -H or -(C=O)CH3

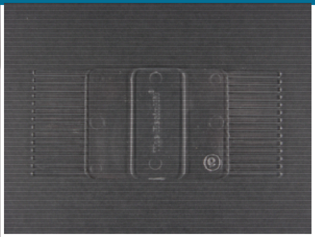
CAB

R= -H or -(C=O)CH3 -(C=O)CH2CH2CH3

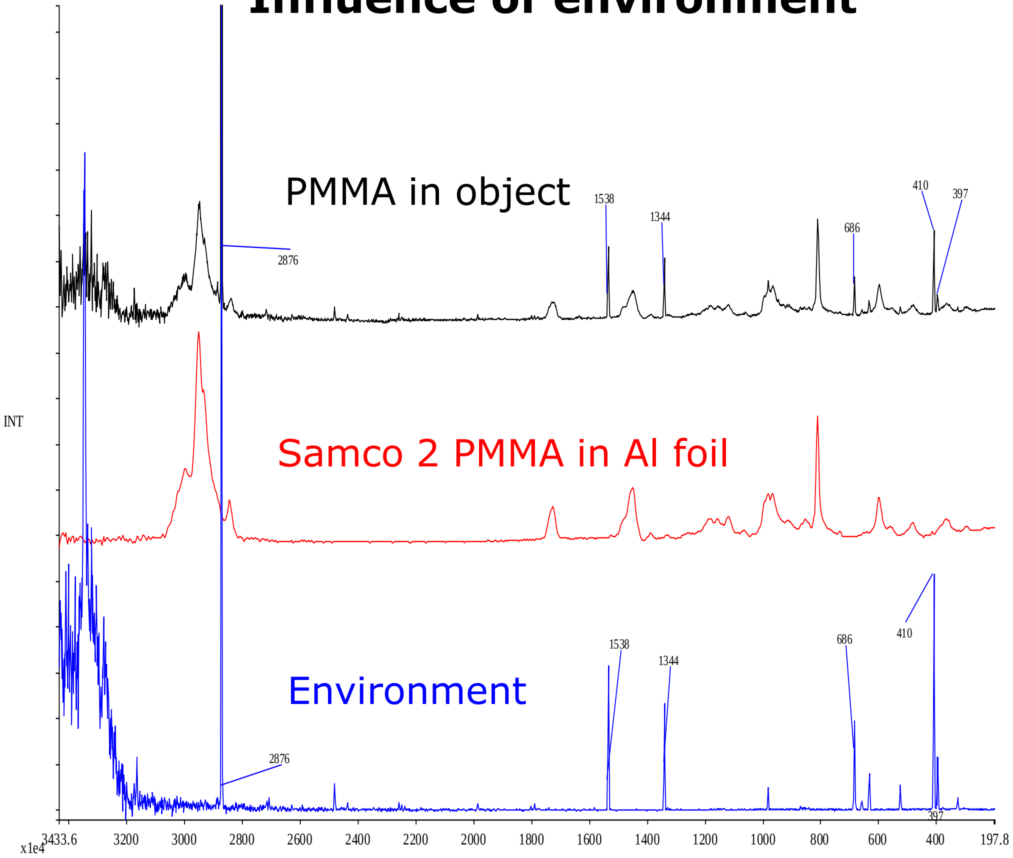




Challenges



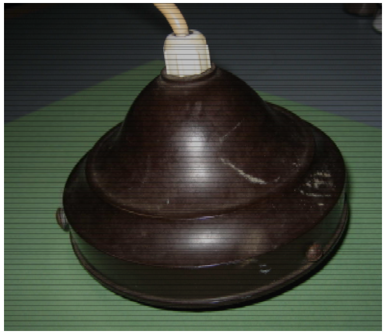
Influence of environment

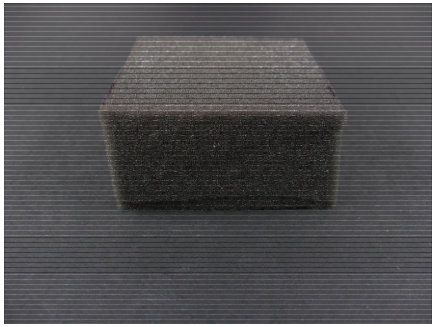


Challenges

Difficult to identify

- Urea formaldehyde (UF)
- Phenol formaldehyde (PF)
- Foamed materials:
  PUR
- Natural materials:
  Horn, Ivory, Tortoise shell
- heavy filled plastics
- black coloured plastics



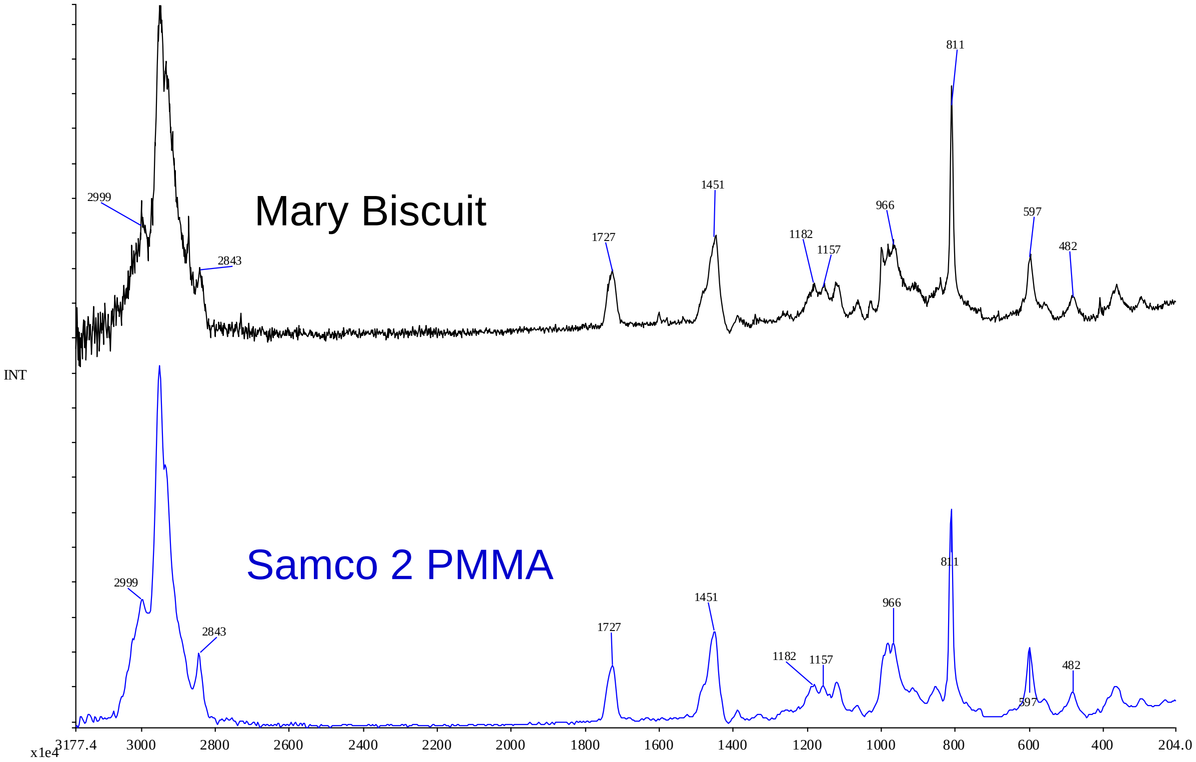


Round Robin

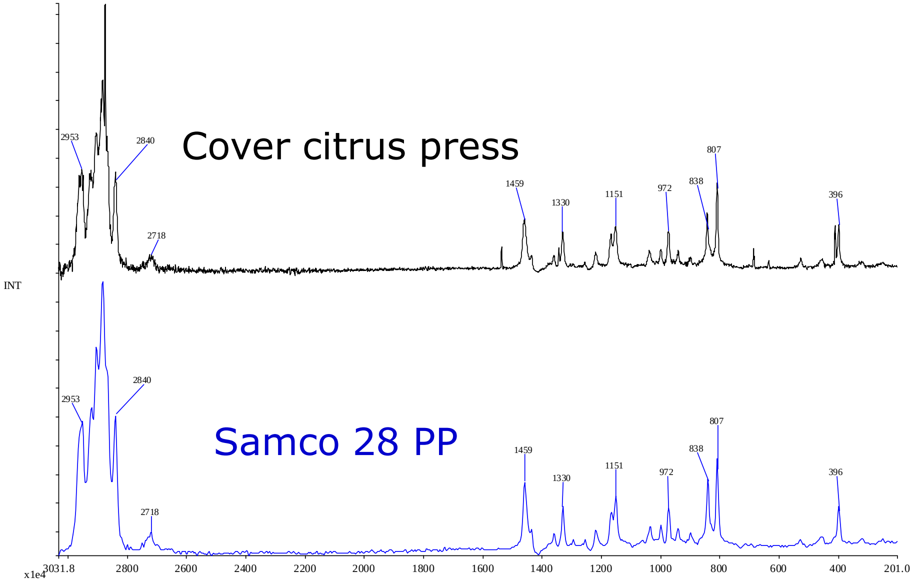
35 test samples in round robin test:

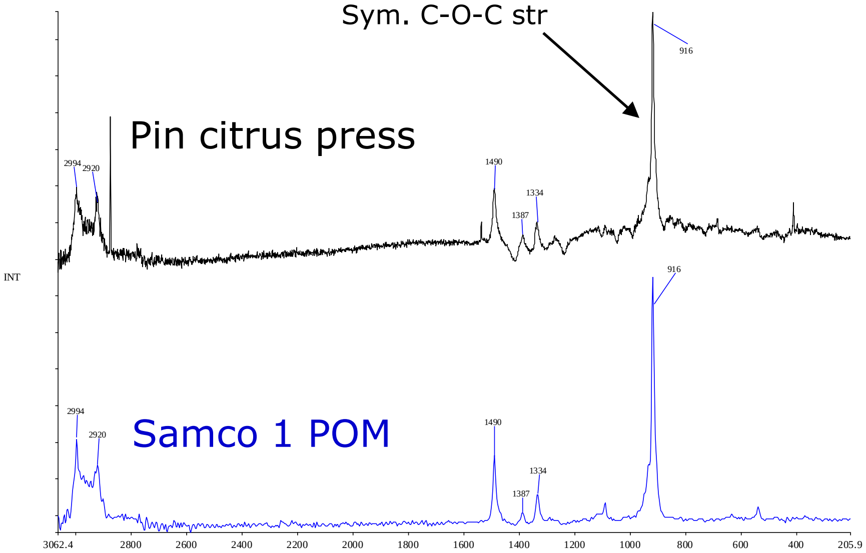
- 22 (63%) identified
- 13 not identified of which 7 black samples and 2 foams
- 2 black samples and 1 foam identified
- burned holes in 3 black samples

From Samco to design objects

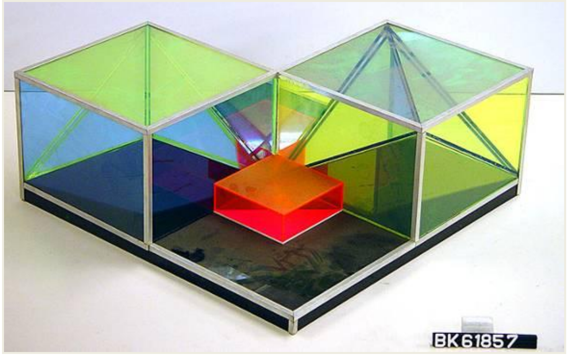


From Samco to design objects

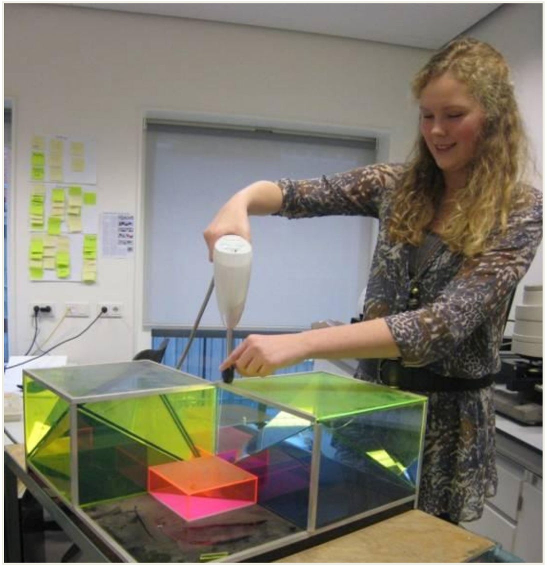


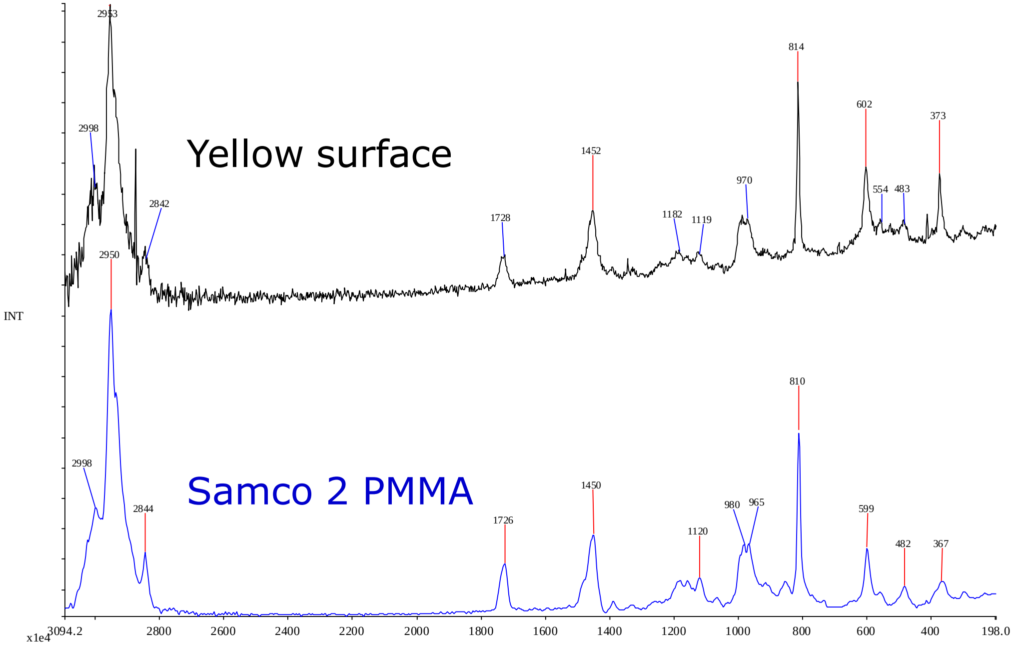


From Samco to Works of Art from RCE study collection



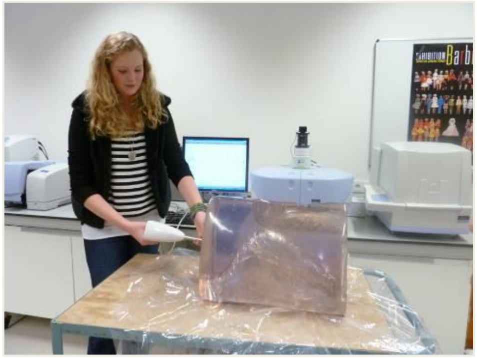
H. E. Kanmeyer, *Nr. III: Geometrische Kompositie*,1978, RCE study collection



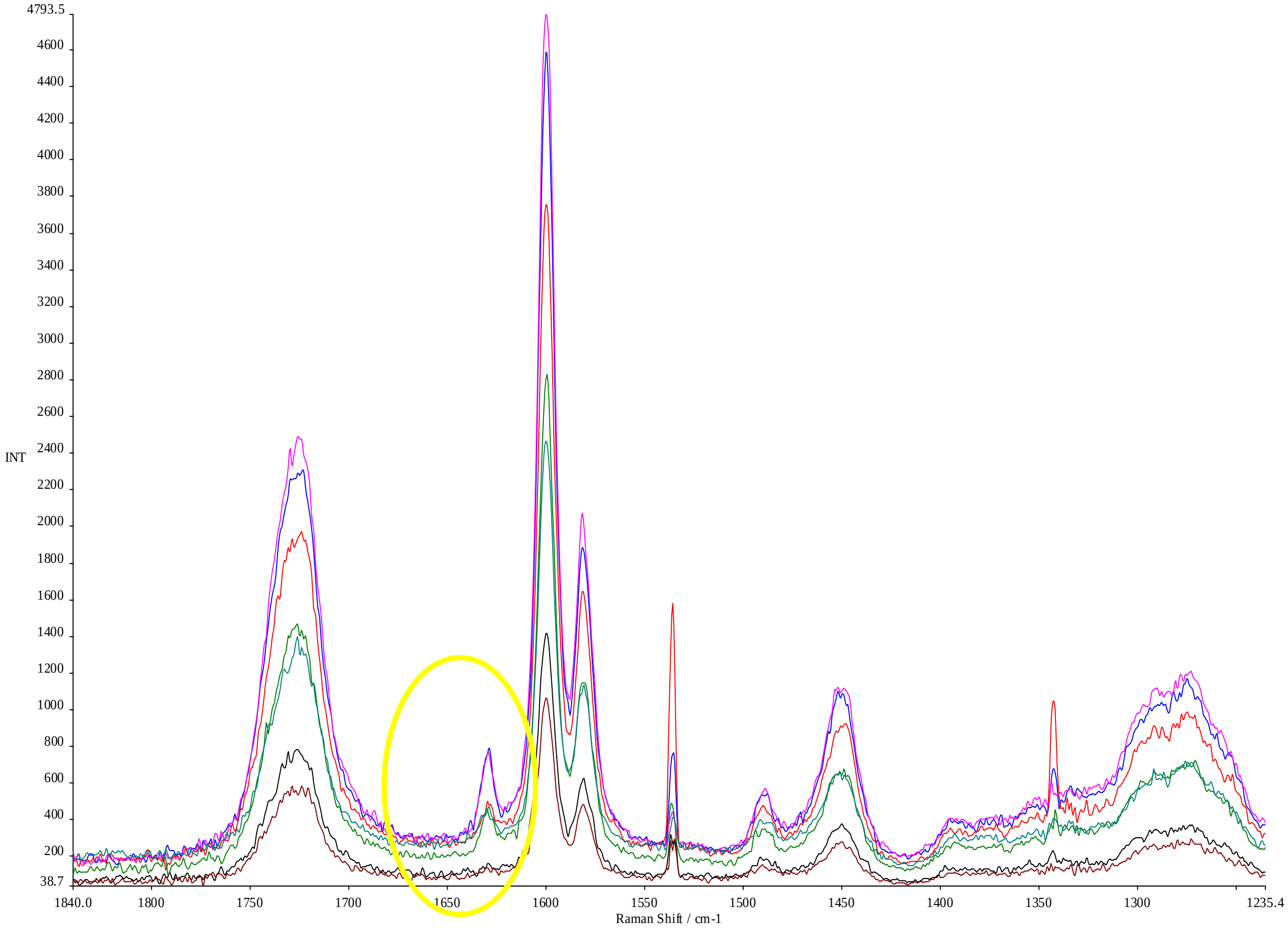


From Samco to Works of Art from RCE study collection

H.O. de Moor, *Untitled*,
RCE study collection

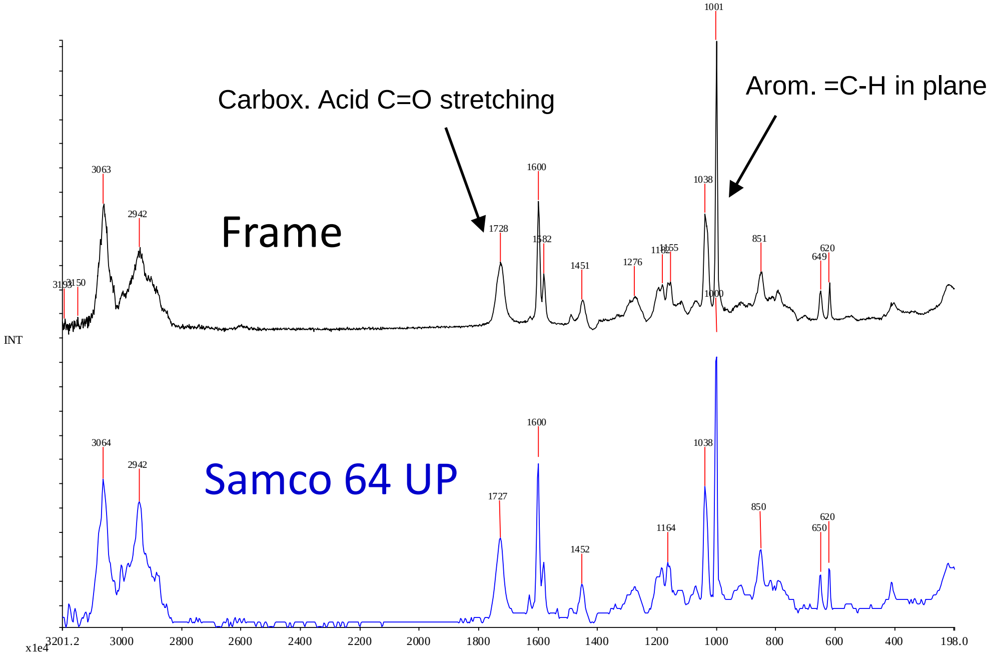


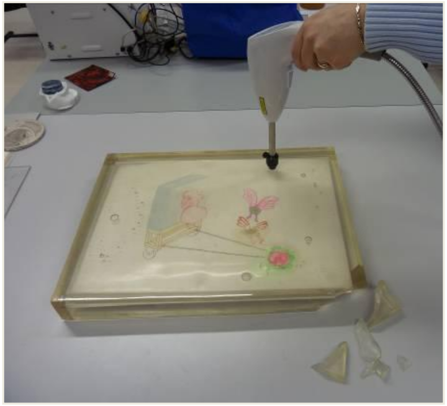
Spectra of the various UP layers



From study collection to works of art

Mathilde ter Heijne, ‘Untitled’, 1993, Océ





From study collection to works of art

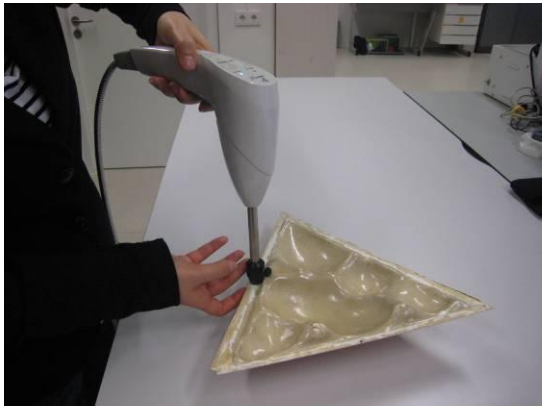
1967

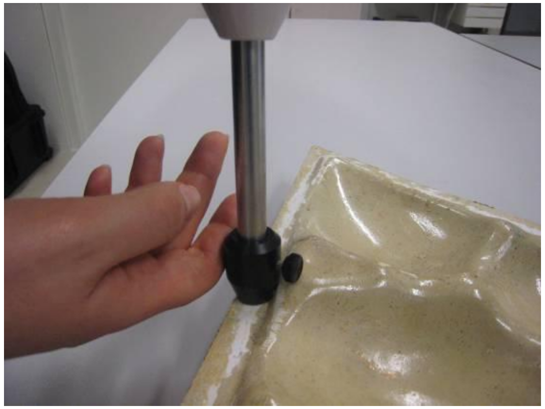
Mathieu J. L. Ficheroux

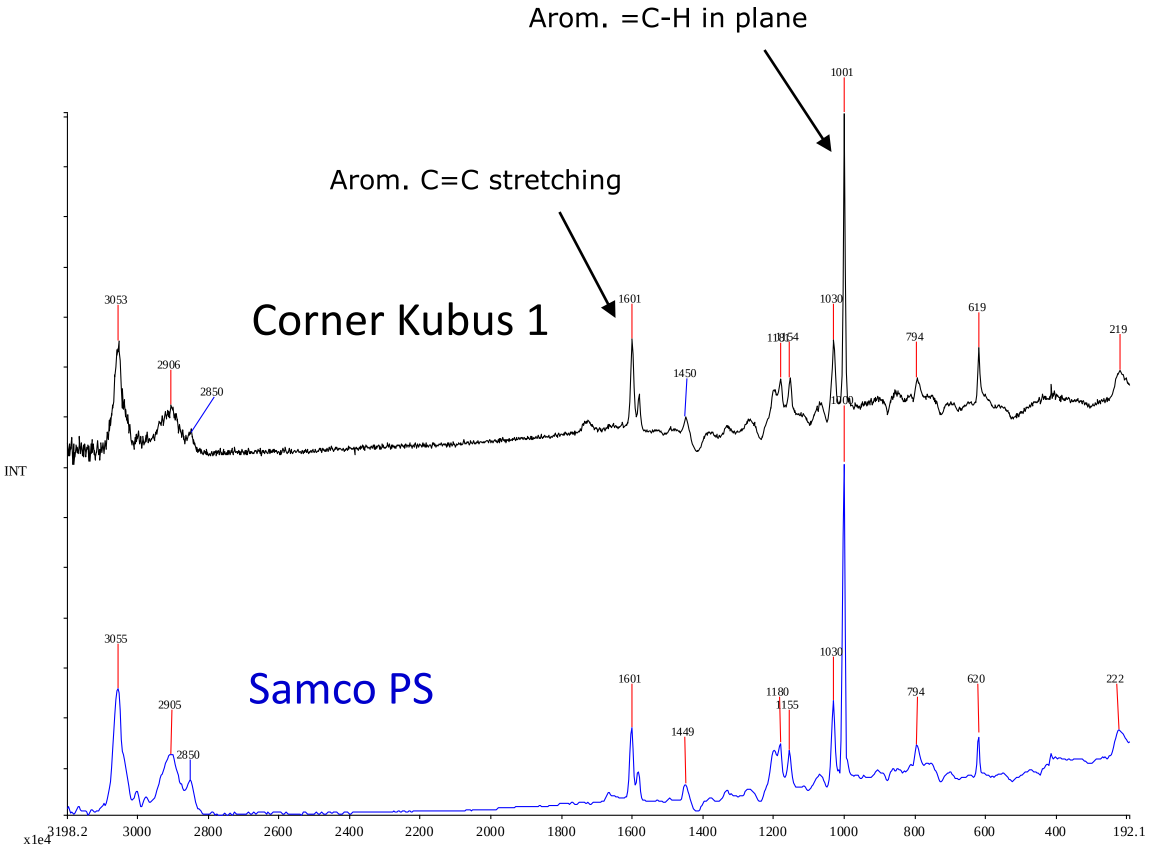
‘2 kubussen’, 1967

2012

From study collection to works of art







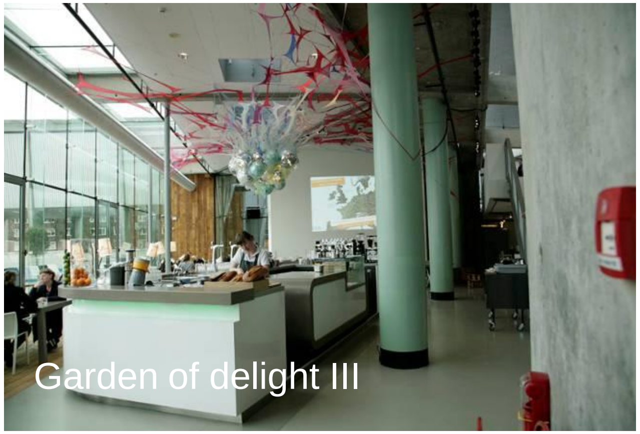
Arom. =C-H in plane

Arom. C=C stretching

From study collection to works of art

Madeleine Berkhemer

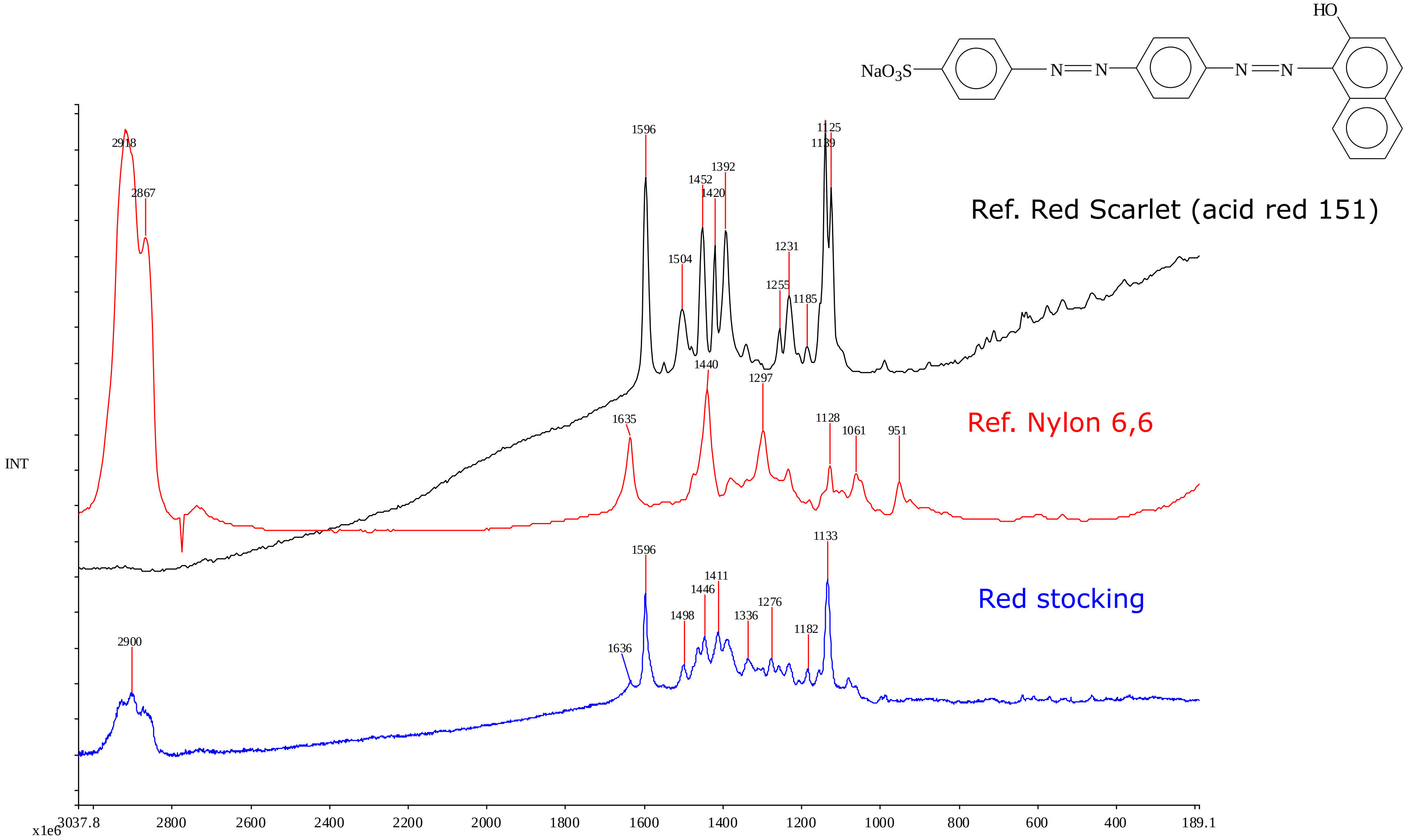
Milly's chandelier



Garden of delight III

Milly’s Maserati

Study for Ghibli'Palais Thum & Taxis



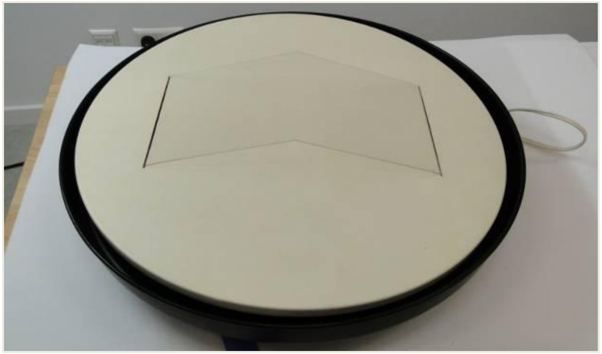
Ref. Red Scarlet (acid red 151)

Ref. Nylon 6,6

Red stocking

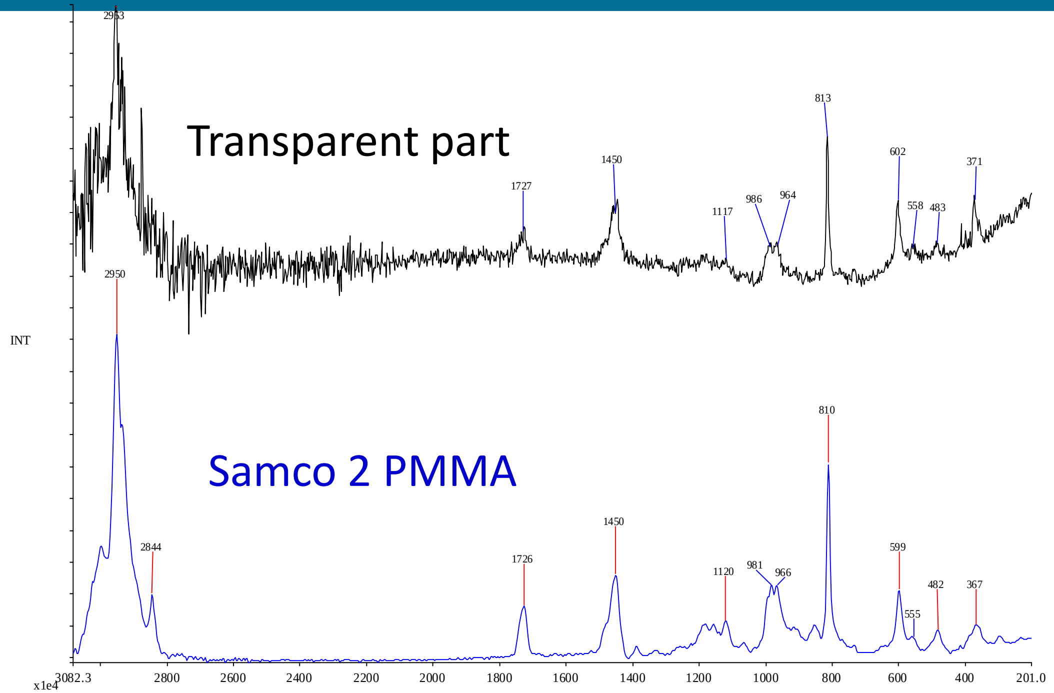
Analyzing works of art in situ

Analyzing works of art in situ



Gabriele de Vecchi, ‘Deformazione Assonometrica’, 1966

Stedelijk Museum Amsterdam



Conclusions

Raman fibre optic probe:

- **modern art objects analysed non invasively,**
- **composition of various plastics in objects identified**
- **many plastics can be identified in short time span**
- **pristine surfaces**
- **works of art which are difficult to access**

difficult to identify (but not impossible):

- **urea formaldehyde,**
- **phenol formaldehyde,**
- **heavy filled plastics,**
- **foamed materials, black coloured plastics**

- **horn, ivory, tortoise shell**

Reference spectra

Raman and FTIR spectra of SamCo will be made available for

IRUG

Acknowledgements

Anna Laganá, Ron Kievits,
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PerkinElmer Nederland

Nicole Delissen,
Sandra Weerdenburg,
Rebecca Timmermans,
Stedelijk Museum Amsterdam

Claudine Helweg,
Océ

Nikki van Basten,
Universiteit van Amsterdam

Madeleine Berkhemer

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman analysis of paintings, photographs, & works of art on paper

Silvia Centeno

Metropolitan Museum of Art, New York, US

FRIDAY, SEPTEMBER 28: LECTURE 6

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Raman analysis with portable instruments

Constanza Miliani

University of Perugia, IT

FRIDAY, SEPTEMBER 28: LECTURE 7

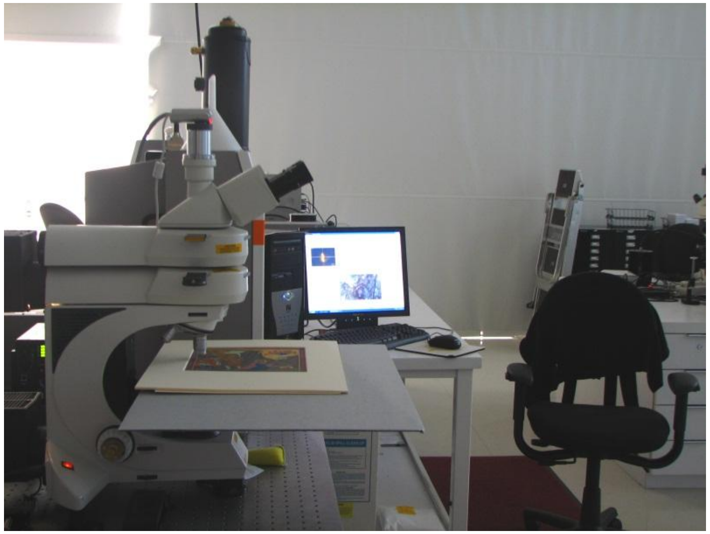
The art of on-site Raman spectroscopy

Costanza Miliani

ISTM-CNR & SMAArt UNIPG, Perugia, ITALY

n.i. off-site

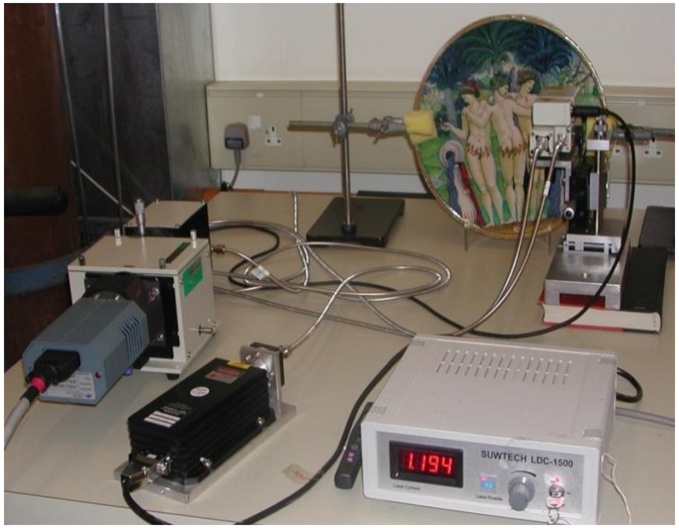
Micro Raman spectroscopy at IRPA/KIK's laboratory



Micro Raman spectroscopy at GCI's laboratory

n.i. on-site

MOLAB micro-Raman at Trevi Church



MOLAB micro-Raman at the Victoria and Albert Museum

Outline

1. Motivations and the context: the MOLAB
2. Portable equipment: issues and limitations
3. Identification of pigments: Raman & other techniques
4. Lead antimonate yellows: $Pb_2Sb_{2-x}\,Y_xO_{7-x/2}$ Y = Zn, Sn
5. Chrome yellows: $PbCrO_4$, $PbCrO_4 \cdot xPbO$, $PbCrO_4 \cdot xPbSO_4$
6. Suppression of fluorescence: SERS

MOLAB equipment

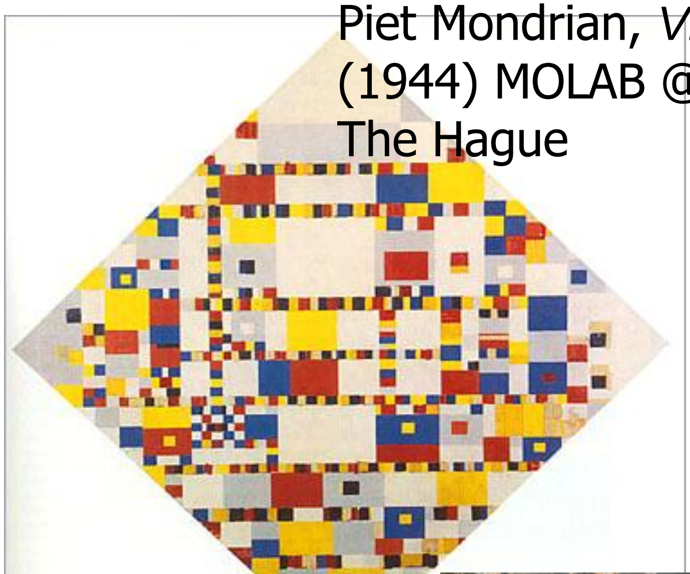
XRF
Raman
Mid-FTIR
Near-FTIR
MOUSE
UV-vis absorption
UV-vis emission
UV-vis time decay
X-ray diffraction
AFM
Video microscopy
UV-vis imaging
Multi-NIR-scanning

CHARISMA

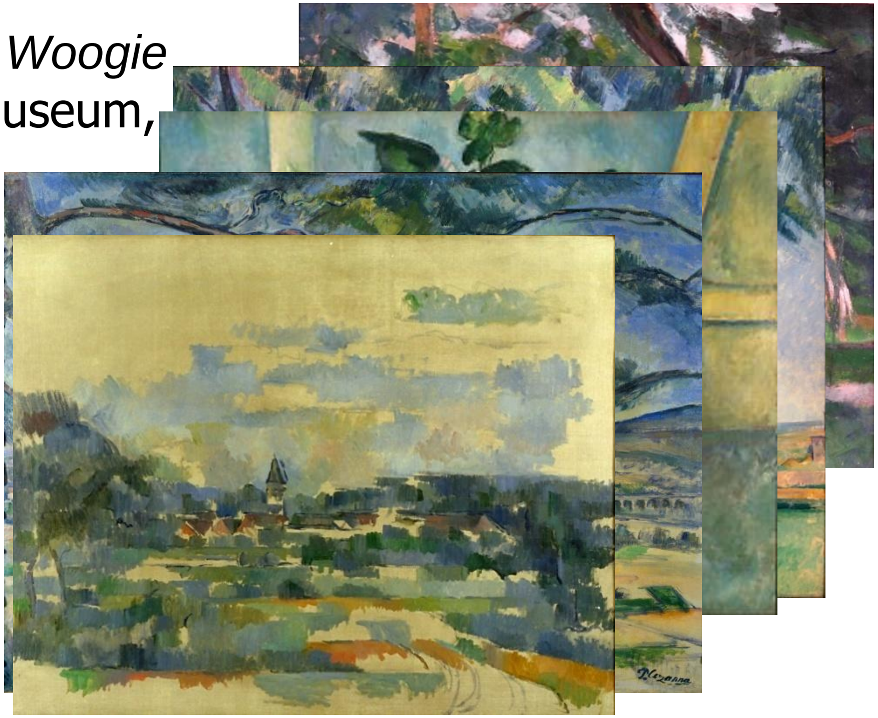
www.charismaproject.eu

SEVENTH FRAMEWORK PROGRAMME

…..Paintings which cannot be sampled



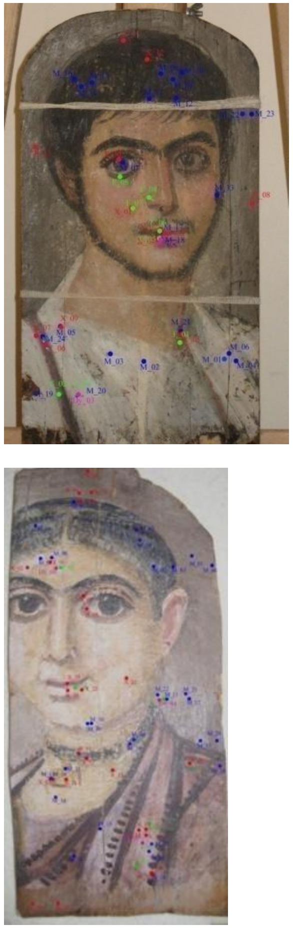
Piet Mondrian, *Victory Boogie Woogie* (1944) MOLAB @ Gemeentemuseum, The Hague



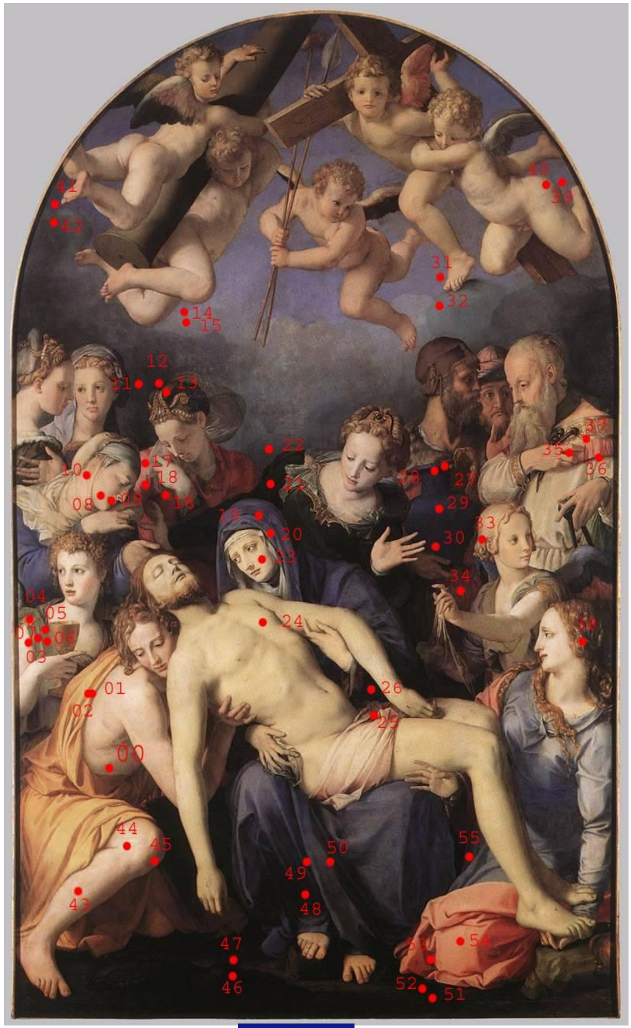
P. Cezanne,
(1875-1902)
MOLAB @ Courtauld, London

Raphael,
The Madonna of the Goldfinch
(1505)
MOLAB @ OPD, Florence

2. Paintings where sampling is limited



Mummy's portraits
 MOLAB @ Carslberg
Glyptotek
Copenhagen



Bronzino,
Lamentation on the dead Christ
(1543)
MOLAB @ Museum of fine Arts, Besancon

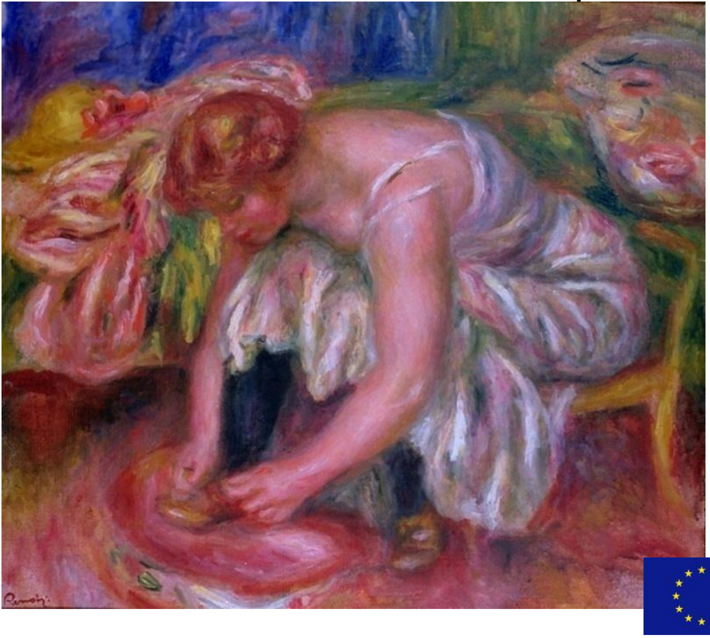
Vasari,
(1500)
MOLAB @ Arezzo

3. Paintings with very high heterogeneity

H. Memlings, Christ surrounded by Angels , MOLAB @ Royal Museum of fine Arts Antwerp

The **macro & micro-scale heterogeneity** of paintings implies that the results obtained on minute samples by means of **bulk or micro-analysis cannot straight generalized to the entire objects.**

The great advantage of **non-invasive methods** is that no contact or sampling is necessary and therefore all the areas of the painting can be examined without any limitation, finally obtaining information on chemical composition and structure **that are statistically representative of the entire artwork.**



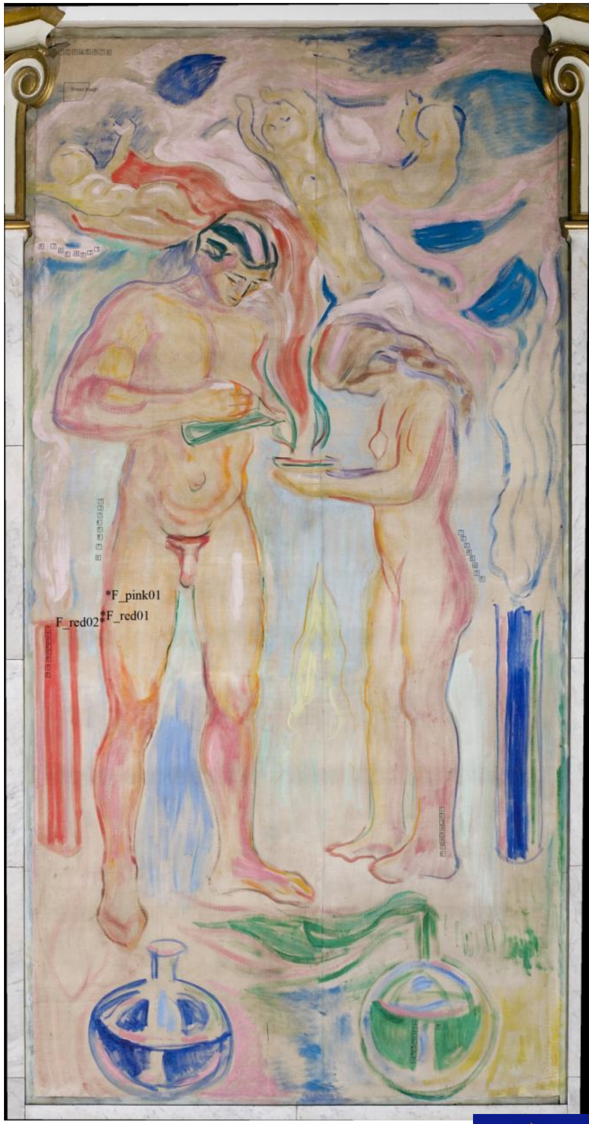
Renoir, W*oman tying her shoe* (c. 1919) MOLAB @ Courtauld, UK

4. Paintings presenting conservation issues

Antonello da Messina,
Ritratto di Trivulsio (1476)
MOLAB @ OPD, Florence.

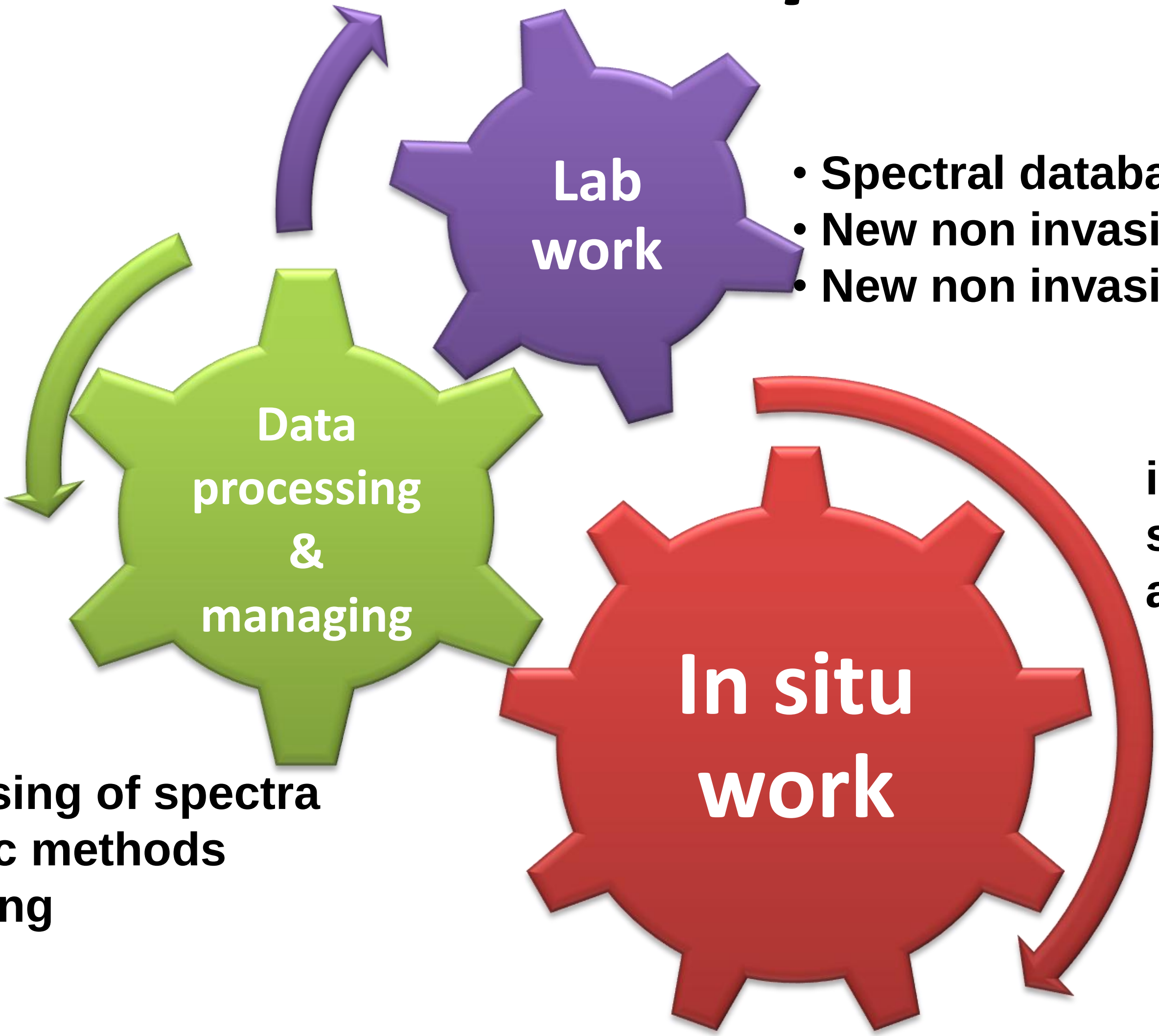
***in-situ* spectroscopic monitoring** may have noteworthy consequences upon the delicate procedure of painting cleaning. **The molecular information that may be immediately provided** adds to the knowledge from which a conservator must draw when **making informed decisions about the best manner in which to proceed**.

Hoyland,
25.4.69
(1969)
MOLAB @ Tate, London.



E. Munch,
Chemistry (1911)
MOLAB @ Oslo University.

MOLAB *modus operandi*



Lab work

Data processing & managing

In situ work

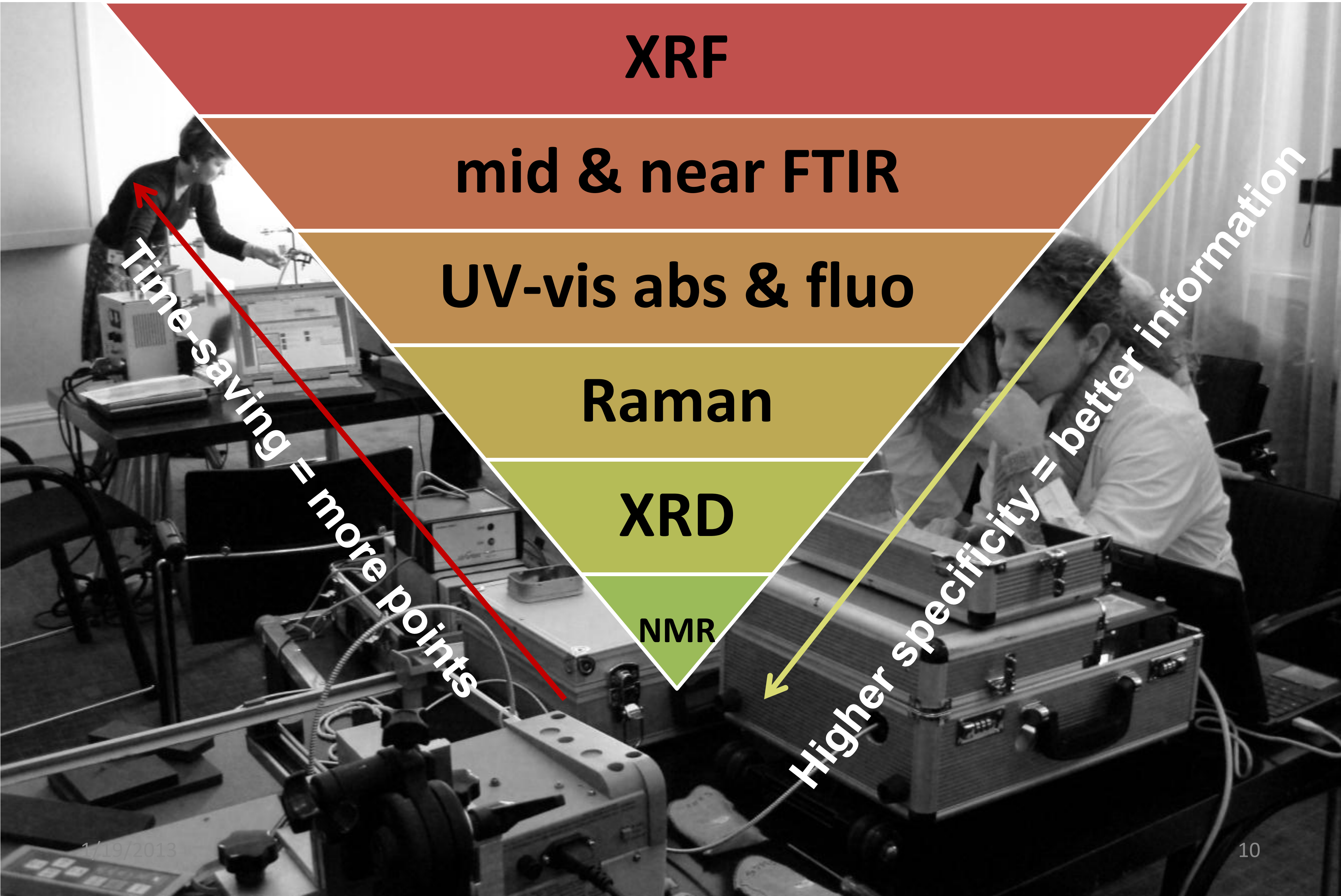
- Spectral databases
- New non invasive methods
- New non invasive techniques

integrated spectroscopic approach

- Post processing of spectra
- Chemometric methods
- Data managing

Miliani C., F. Rosi, B.G. Brunetti, A. Sgamellotti, Account of Chemical Research, 2010

The integrated spectroscopic approach of MOLAB



XRF

mid & near FTIR

UV-vis abs & fluo

Raman

XRD

NMR

Time-saving = more points

Higher specificity = better information

Outline

1. Motivations and the context: the MOLAB

2. Portable equipment: issues and limitations

3. Identification of pigments: Raman & other techniques

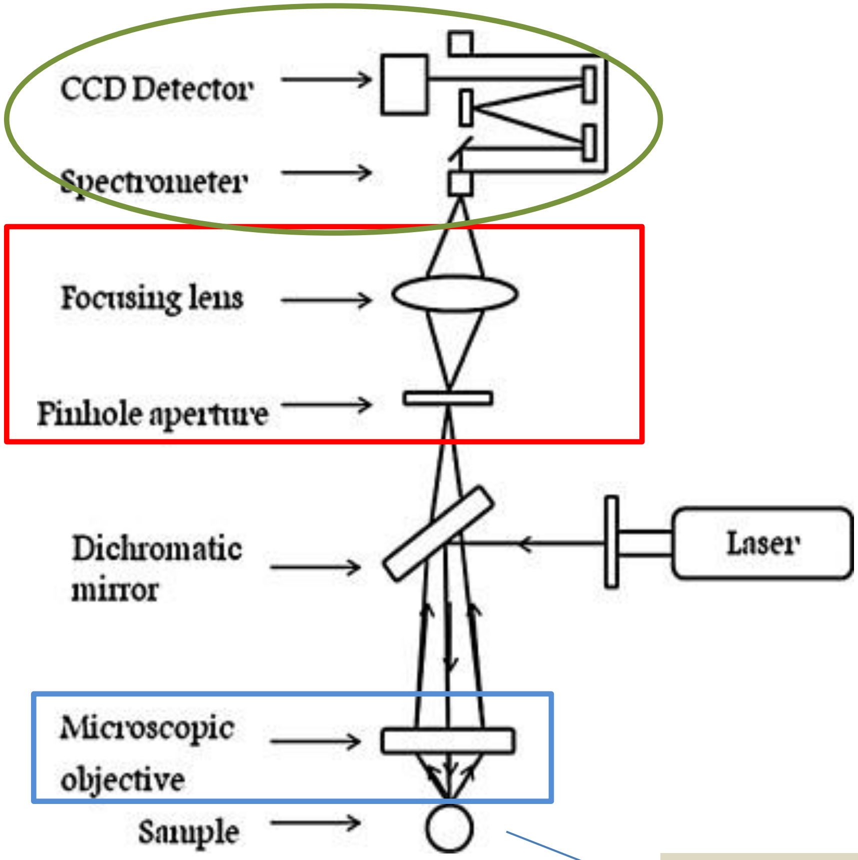
4. Lead antimonate yellows: $Pb_2Sb_{2-x}\,Y_xO_{7-x/2}$

5. Chrome yellows: $PbCrO_4$, $PbCrO_4{\cdot}xPbO$, $PbCrO_4{\cdot}xPbSO_4$

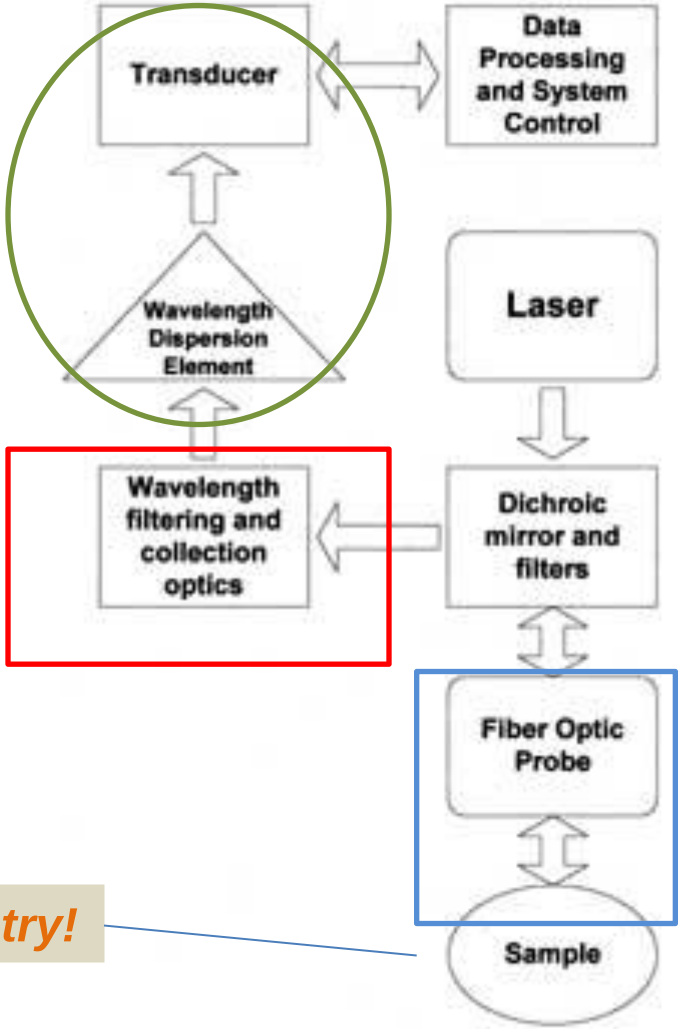
6. Suppression of fluorescence: SERS

Raman spectrometers: from the lab to the museum

off-site



on-site



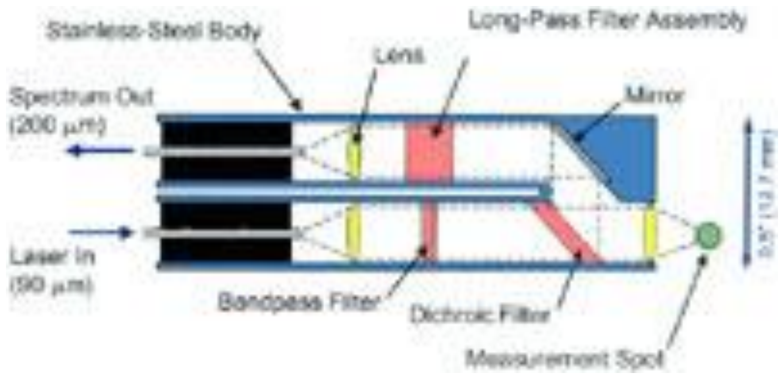
Backscattering geometry!

1. No confocal set up = higher fluorescence background from the matrix
2. No microscopic objective = lower signal/noise ratio
3. Optical path constraints = worst spectral resolution, shorter spectral range

Portable instrument design: major issues

- Laser excitation source: wavelength, power; stability;

going (deep) red or NIR



- Fiber-optic (or remote) probe including working distance, filtering, and remote-shutter control;

Grating 1200-600 lines/mm^{-1}

(no movable components….)

- Optical design including the design of the collection optics and monochromator;

CCD (pixel array size of 1024 x 128 with 2 micrometer pixels)

- Detection system;

Micro and macro positioning, Stable tripod….

- Accessories for field work.

Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta 588 (2007) 108–116
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Comparative study of mobile Raman instrumentation for art analysis

P. Vandenabeele[a,*], K. Castro[b], M. Hargreaves[c], L. Moens[a],
J.M. Madariaga[b], H.G.M. Edwards[c]

[a] *Ghent University, Department of Analytical Chemistry, Proeftuinstraat 86, B-9000 Ghent, Belgium*
[b] *University of the Basque Country (EHU/UPV), Department of Analytical Chemistry, B° Sarriena, s/n, 48940 Leioa, Bizkaia, Spain*
[c] *University of Bradford, Division of Chemical & Forensic Sciences, School of Life Sciences, Bradford BD7 1DP, UK*

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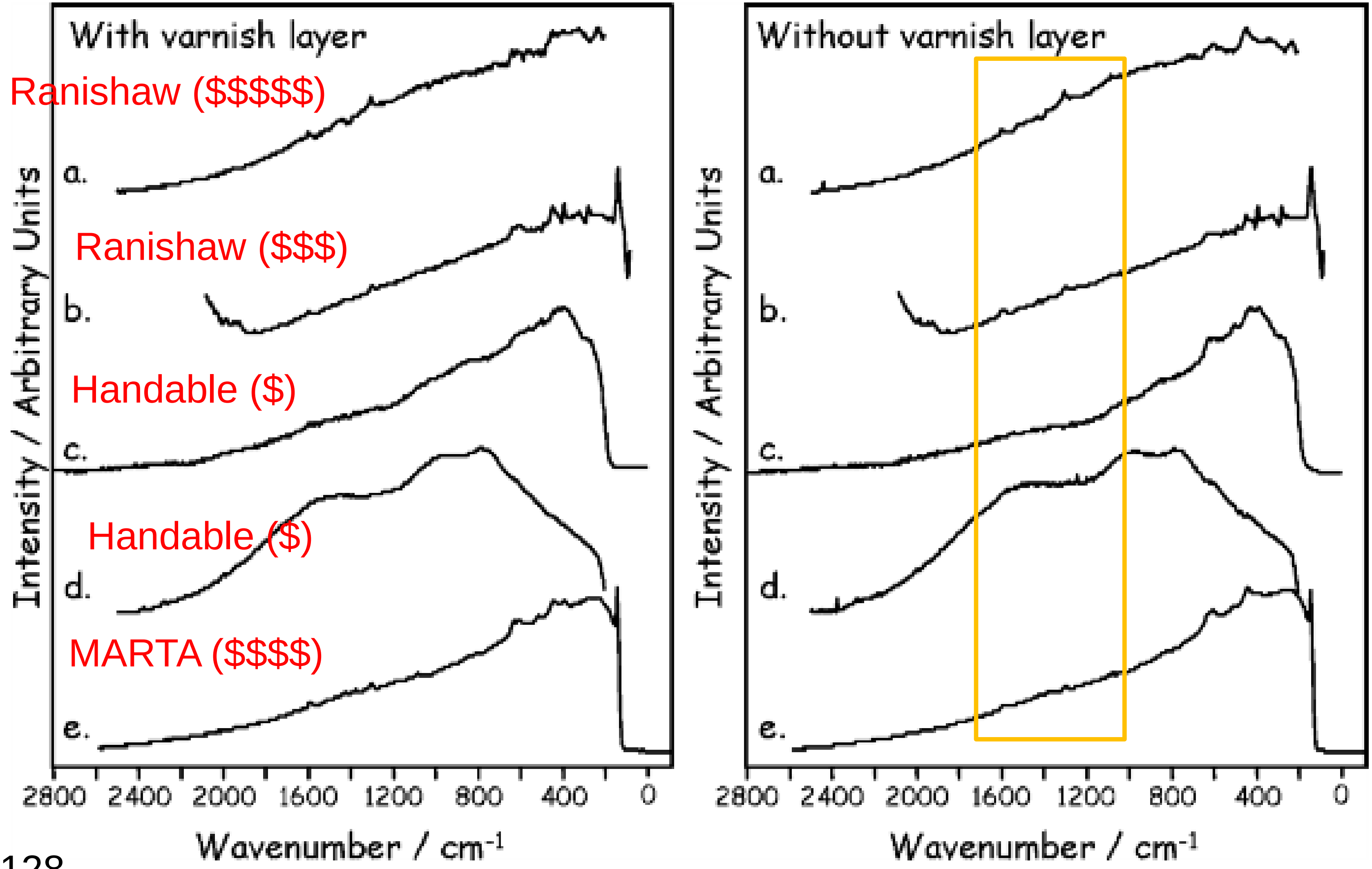
Available online 12 February 2007

Table 2
Overview of some external characteristics of the mobile instrumentation

Characteristic	Renishaw RA100	Renishaw Portable Raman Analyser RX210	Ocean Optics RSL-1	Delta Nu Inspector Raman	Mobile Art Analyser (MArtA)
Weight (kg)	28.1	14.2	2.3 Including computer	2.3	27.5
Dimensions (cm × cm × cm)	67.5 × 52 × 20 + probe head	48.5 × 35.5 × 20 + probe head	13 × 27 × 2 + probe head	17 × 12 × 6.5 + handle	67 × 47 × 35
Positioning equipment	Micro- and macro-positioning (horizontal post, XYZ stage)	Translational stage where required can be used without	–	Translational stage where required can be used without	Micro- and macro-positioning (vertical post, articulating arm, translation stage)
Camera	Colour camera (uses same objective lens)	–	–	Nuscope accessory (colour camera/white light)	Colour camera (uses same objective lens)
Computer	Desktop with TFT screen, through serial port	Laptop, through USB	Mini-laptop, through USB	Mini-laptop, through USB or through wireless	Laptop, through USB and RS-232
Estimated time for set-up (min)	Ca. 15 + 30 of warm-up and calibration	Ca. 10 including silicon calibration	Ca. 5	Ca. 10 including polystyrene calibration	Ca. 30, including wavelength calibration
Grating	1200 lines mm^{-1}	1000 lines mm^{-1}	No information available	No information available	1200 and 600 lines/ mm^{-1}[a]
Detector	400 × 575 CCD	400 × 575 CCD	2048 × 1 linear CCD	1024 × 1 linear CCD	1024 × 512 CCD
Laser	785 nm diode, 500 mW	785 nm diode 500 mW	785 nm diode, 500 mW	785 nm diode, 120 mW	785 nm diode, 300 mW
Instrument price, excl. VAT (€ = ca. 25,000 €)	<ca. €€€€€	<ca. €€€	ca. €	<ca. €	<ca. €€€€

[a] For this study only the 600 lines mm^{-1} dispersion grating was used.



Ranishaw ($$$$$)

Ranishaw ($$$)

Handable ($)

Handable ($)

MARTA ($$$$)

PY128

Fig. 3. Raman spectra of the yellow paint samples, with and without varnish layer, as recorded with the mobile Raman instruments. With varnish layer: (a) Renishaw RA-100 (50 accumulations of 10 s); (b) Renishaw RX–210 (5 accumulations, 10 s); (c) Ocean Optics RSL-1 (1 accumulation of 5 s); (d) Delta Nu Inspector Raman (10 accumulations of 5 s); (e) MArtA (60 accumulations of 10 s); Without varnish layer: (a) Renishaw RA-100 (50 accumulations of 10 s); (b) Renishaw RX-210 (5 accumulations, 10 s); (c) Ocean Optics RSL-1 (1 accumulation of 5 s); (d) Delta Nu Inspector Raman (10 accumulations of 5 s); (e) MArtA(60 accumulations of 10 s).

JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. (2008)
Published online in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/jrs.1941

JRS

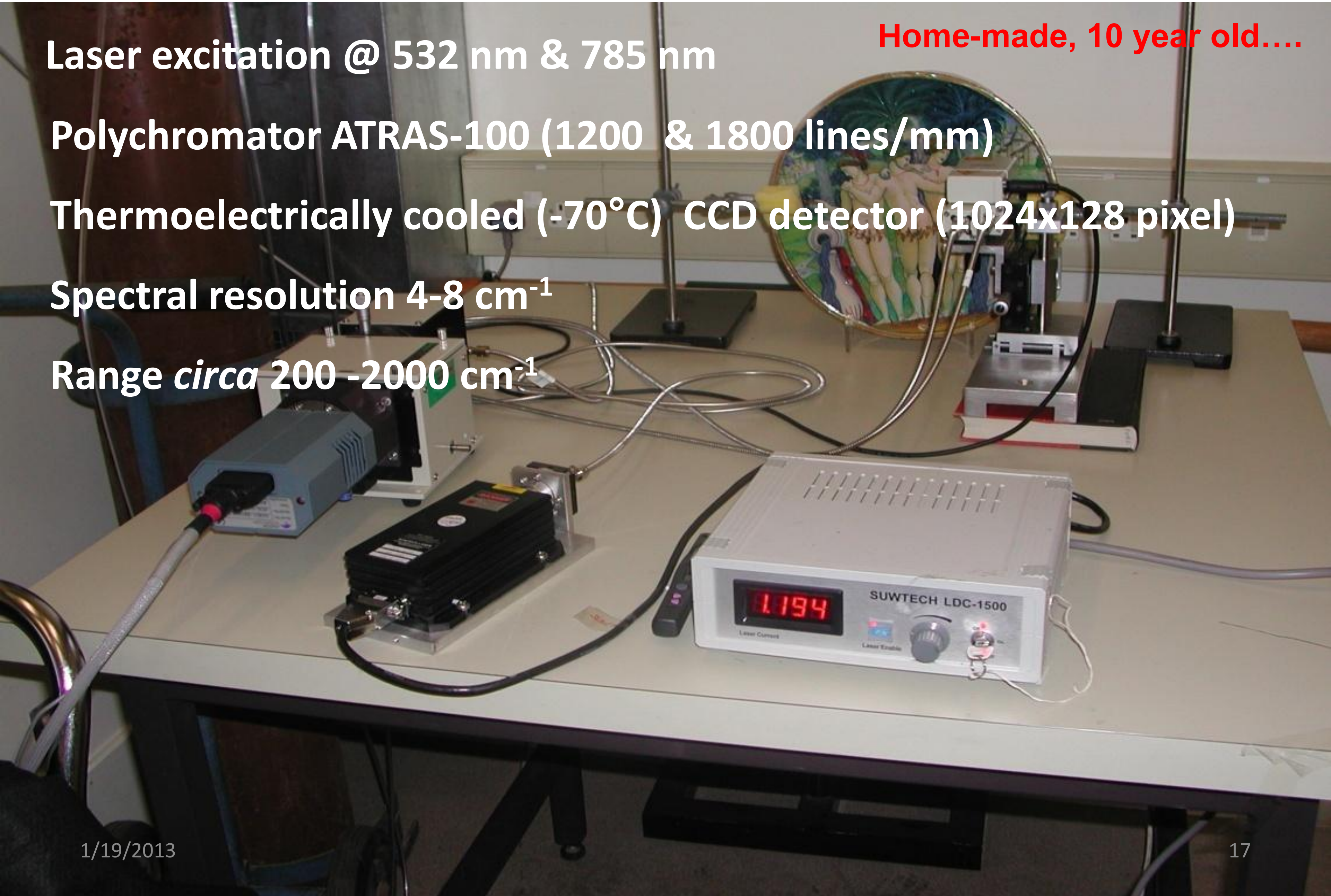
Evaluation of three different mobile Raman microscopes employed to study deteriorated civil building stones

I. Martínez-Arkarazo,[1]* D. C. Smith,[2] O. Zuloaga,[1] M. A. Olazabal[1] and J. M. Madariaga[1]

Characteristic	 DeltaNu Inspector Raman	 BWTEK BWS415 i-Raman	 Renishaw RA100
Weight (kg)	3 ultramobile	2.7 ultramobile	28.1 portable
Dimensions (cm)	17 × 12 × 6.5 + handle	17 × 34 × 23.5 + probe head	67.5 × 52 × 20 + probe head
			Project Chapter / Article #
Excitation wavelength (nm)	785	785	785
Laser power at the source (mW)	40 fixable at 3 levels	300 non-changeable[a]	500 variable at 1, 10 and 100%
Highest spectral resolution (cm^{-1})	10[b]	5–6	4
Spectral range (cm^{-1})	200–2000	175–3100	200–4000
Focusing	A pointing accessory and the NuScope microscope video accessory (in colour)	A pointing accessory	Colour microcamera with 5×, 20× and 50× objective lens
Data acquisition software	NuSpec (DeltaNu, Wyoming, USA)	BWSpec, GRAMS (Galactic Industries, Salem, NH, USA)	Spectracalc, GRAMS (Galactic Industries, Salem, NH, USA)

[a] A software-based mechanism is being implemented to allow changing the laser power.
[b] This spectrometer can now descend till 100 cm^{-1}, and a better spectral resolution is possible as well.

MOLAB: portable (micro)-Raman equipment



Home-made, 10 year old….

Laser excitation @ 532 nm & 785 nm

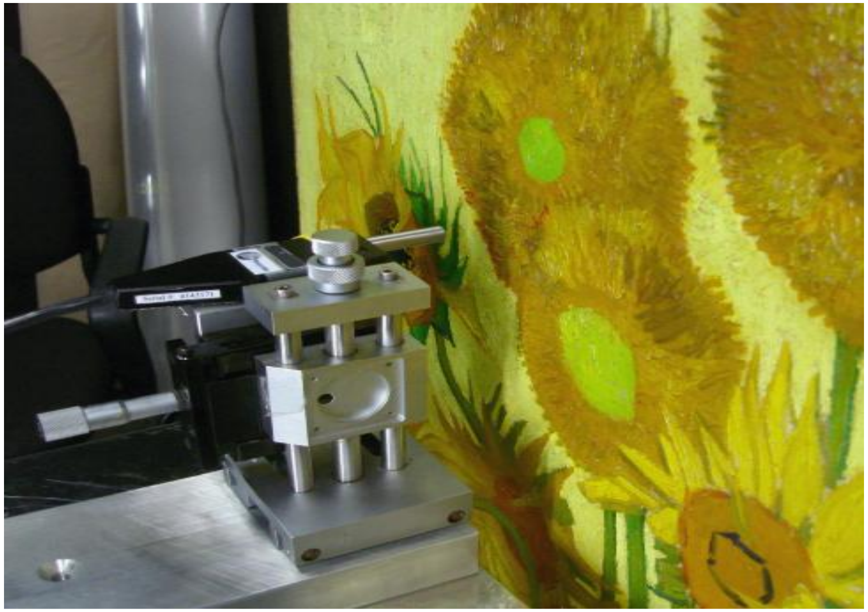
Polychromator ATRAS-100 (1200 & 1800 lines/mm)

Thermoelectrically cooled (-70°C) CCD detector (1024x128 pixel)

Spectral resolution 4-8 cm^{-1}

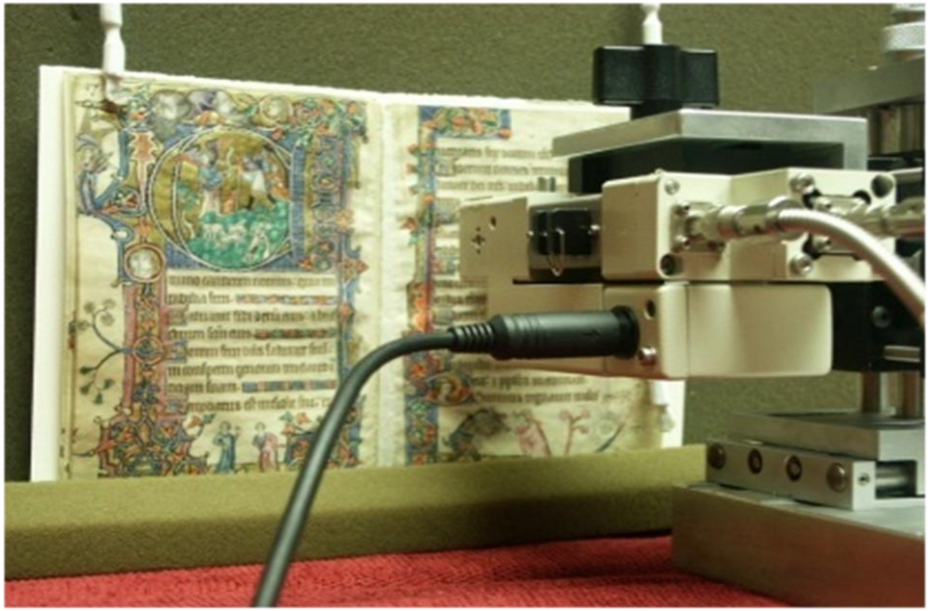
Range *circa* 200 -2000 cm^{-1}

Fiber optic probe

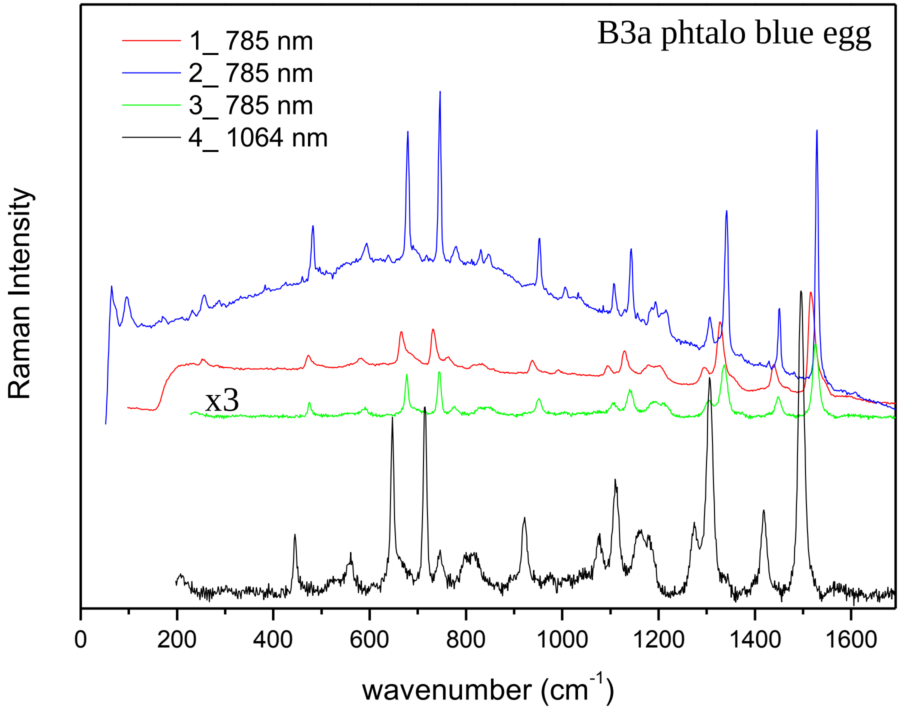


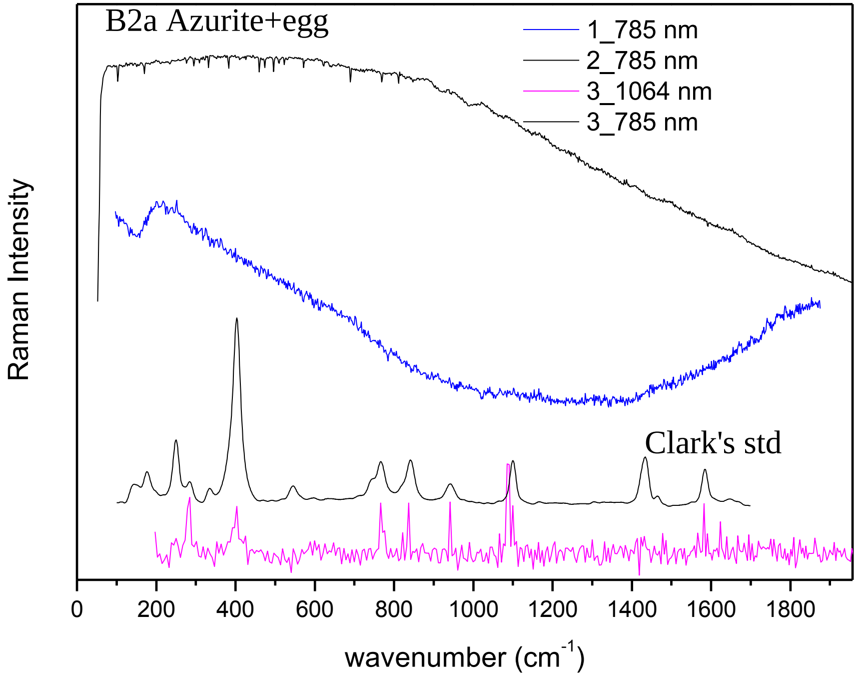
Working distance:7.5 mm
Spectral range 250-3900 cm^{-1}
Permanently-aligned combination of two single fibers (105 μm excitation fiber, 200 μm collection fiber standard) with filtering and steering micro-optics, N.A. 0.22
Laser excitation @ 785 nm

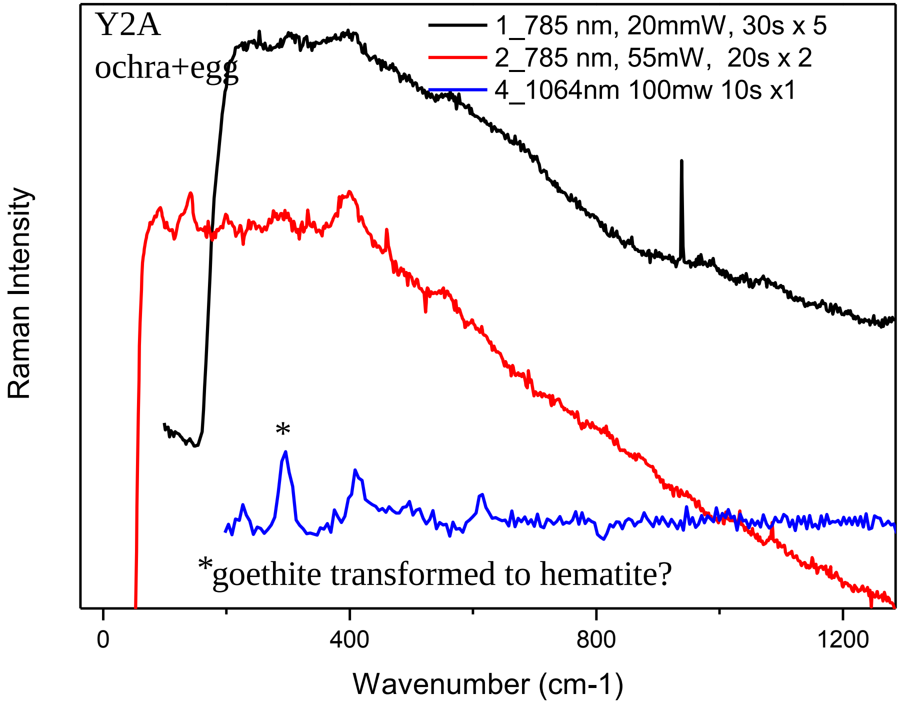
Micro-probe



RMP micro-probe (25x 50x)
LWD objectives
Working distance 10 mm
CCD videocamera for the sample centering
Notch filters
Spectral range 200-3900 nm
Laser excitation @ 532 nm & 785 nm







1_ 785 nm , fiber optics, home-made (res=6 cm^{-1}, range 250-2000) MOLAB

2_ 785 nm, fiber optics B&WTEK (res=3 cm^{-1}, range:175 -1800)

3_ 785 nm, fiber optics RIGAKU (res=8 cm^{-1}, range 200-2000)

4_ 1064 nm, fiber optics RIGAKU (res=8 cm^{-1}, range 200-2000)

On-site Raman measurements: major issues

- **Ambient (Day, Room, PC) light;**
- **Vibration (scaffolding/easel/object) and defocusing;**
- **Fluorescence of the matrix;**
- **Photo/thermal bleaching.**

Anal Bioanal Chem (2005) 383: 707–712
DOI 10.1007/s00216-005-0045-2

ORIGINAL PAPER

Peter Vandenabeele · Karel Lambert · Sofie Matthys ·
Walter Schudel · Anna Bergmans · Luc Moens

In situ analysis of mediaeval wall paintings: a challenge for mobile Raman spectroscopy

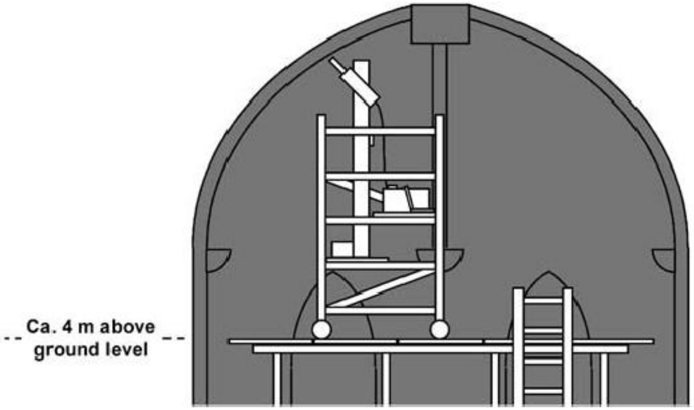


Fig. 2 Schematic overview of the experimental set-up for the analysis of mediaeval wall paintings on the ceiling of the chapel of Ponthoz

Review

Journal of RAMAN SPECTROSCOPY

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(wileyonlinelibrary.com) DOI 10.1002/jrs.4042

The on-site/remote Raman analysis with mobile instruments: a review of drawbacks and success in cultural heritage studies and other associated fields†

Philippe Colomban*

Successful studies….

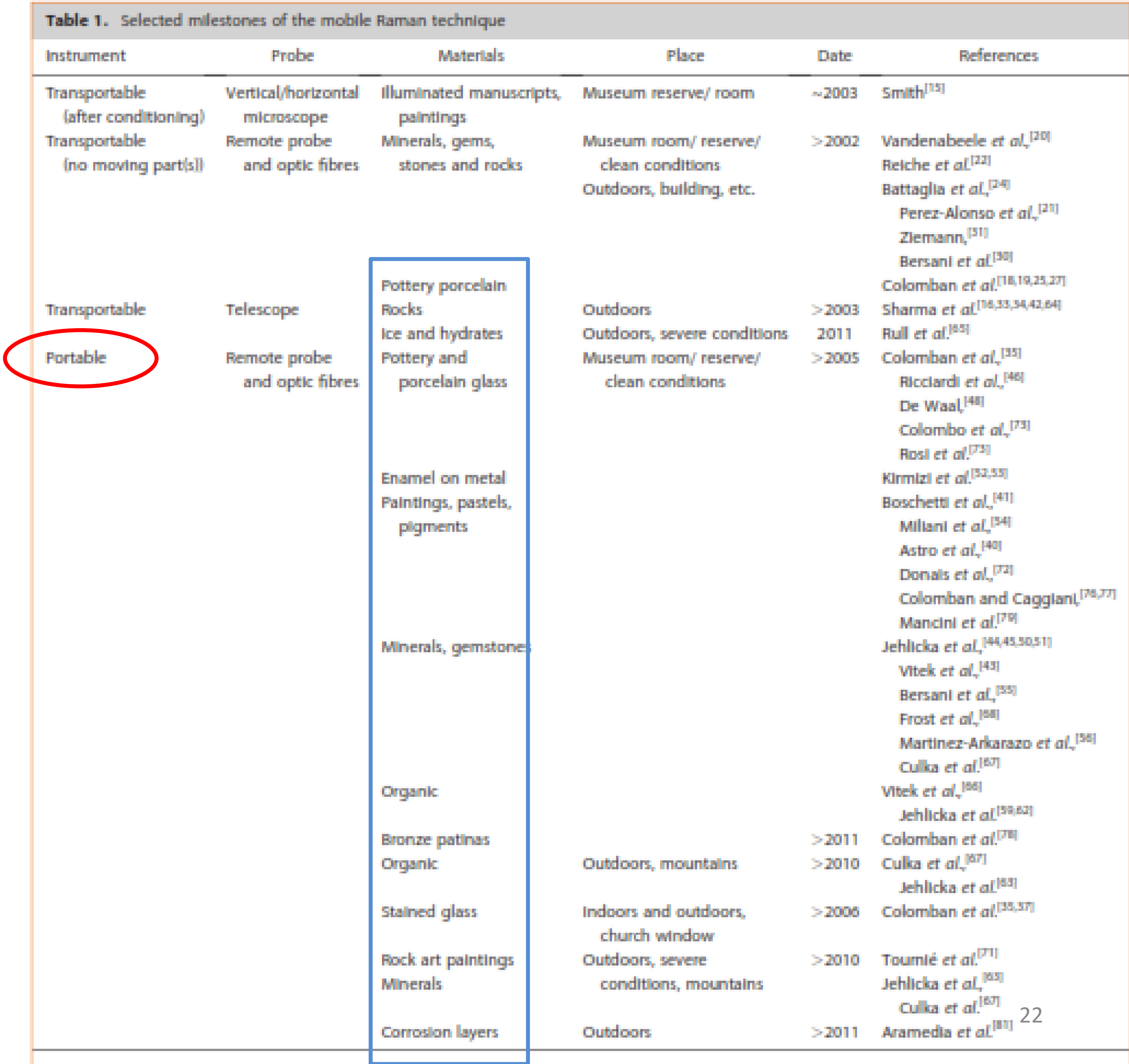


Table 1. Selected milestones of the mobile Raman technique

Instrument	Probe	Materials	Place	Date	References
Transportable (after conditioning)	Vertical/horizontal microscope	Illuminated manuscripts, paintings	Museum reserve/ room	~2003	Smith[15]
Transportable (no moving part(s))	Remote probe and optic fibres	Minerals, gems, stones and rocks	Museum room/ reserve/ clean conditions Outdoors, building, etc.	>2002	Vandenabeele et al.,[20] Reiche et al.[22] Battaglia et al.,[24] Perez-Alonso et al.,[21] Ziemann,[31] Bersani et al.[30]
		Pottery porcelain			Colomban et al.[18,19,25,27]
Transportable	Telescope	Rocks	Outdoors	>2003	Sharma et al.[18,33,34,42,64]
		Ice and hydrates	Outdoors, severe conditions	2011	Rull et al.[65]
Portable	Remote probe and optic fibres	Pottery and porcelain glass	Museum room/ reserve/ clean conditions	>2005	Colomban et al.,[35] Ricciardi et al.,[46] De Waal,[48] Colombo et al.,[73] Rosi et al.[73]
		Enamel on metal			Kirmizi et al.[52,53]
		Paintings, pastels, pigments			Boschetti et al.,[41] Milani et al.,[54] Astro et al.,[40] Donais et al.,[72] Colomban and Caggiani,[76,77] Mancini et al.[79]
		Minerals, gemstones			Jehlicka et al.,[44,45,50,51] Vitek et al.,[43] Bersani et al.,[55] Frost et al.,[68] Martinez-Arkarazo et al.,[56] Culka et al.[67]
		Organic			Vitek et al.,[66] Jehlicka et al.[59,62]
		Bronze patinas		>2011	Colomban et al.[78]
		Organic	Outdoors, mountains	>2010	Culka et al.,[67] Jehlicka et al.[63]
		Stained glass	Indoors and outdoors, church window	>2006	Colomban et al.[35,37]
		Rock art paintings	Outdoors, severe conditions, mountains	>2010	Tournié et al.[71]
		Minerals			Jehlicka et al.,[63] Culka et al.[67]
		Corrosion layers	Outdoors	>2011	Aramedia et al.[81]

Outline

1. Motivations and the context: the MOLAB

2. Portable equipment: issues and limitations

3. **Identification of pigments: Raman & other techniques**

4. Lead antimonate yellows: $Pb_2Sb_{2-x} Y_xO_{7-x/2}$

5. Chrome yellows: $PbCrO_4$, $PbCrO_4 \cdot xPbO$, $PbCrO_4 \cdot xPbSO_4$

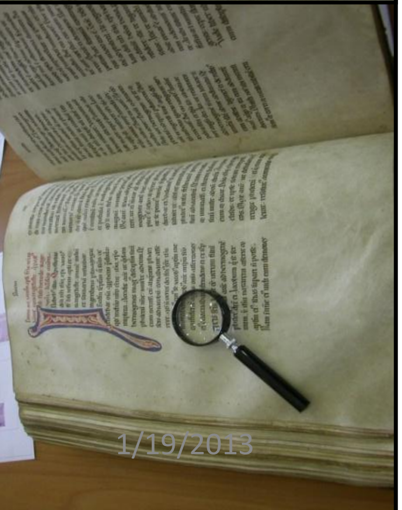
6. Suppression of fluorescence: SERS

Non invasive on-site pigment ID

	FTIR[1]	Raman	XRD[2]
Instrumental restriction	**Very low: portable are now good as bench top**	High: smaller range, worst spectral and spatial resolution	High: smaller range, worst spectral resolution
Time of measurement	Fast (≈1-3’)	Long (≈5-10’)	**Very long (≈20-30’)**
Matrix effect	Small (to avoid overlapping, it’s better go for combo bands)*	**Large, a lot of fluorescence especially in ancient painting!**	Medium (high in case of high XR absorbing extender i.e. biacca)
Spectral distortion	**A lot! (derivative & reststralen band)*** **Transmission data base cannot be used**	**NO**	**Some (pick shift)** **After internal calibration database can be used for assignment.**
Varnish	It’s a problem	Little problem (thermal degradation)	No problem

[1] *Miliani et al., Applied Physics A, 2011*

[2] *Eveno et al., Applied Physics A, 2010*



Portuguese Medieval manuscripts from *SANTA CRUTZ* (XII-XIII AC)

BLU	**Lapis (Raman + FTIR)**
	Indigo & lead white (FTIR + UV-vis fluo)
	Lapis & indigo (Raman + FTIR + UV-vis fluo)
GREEN	**Cu, Zn, Ca oxalate (XRF + FTIR)**
	Orpiment & indigo (XRF + Raman + UV-vis fluo)
YELLOW	**unknown fluorescent dye (XRF + UV-vis fluo)**
	Orpiment (XRF + Raman)
ORANGE	**Cinnabar + orpiment (XRF + Raman)**
RED	**Minium (Raman)**
	Cinnabar (Raman)
	Cinnabar & organic dye (Raman + UV-vis fluo)
PURPLE-VIOLET	**Anthraquinonic dyes (UV-vis fluo)**

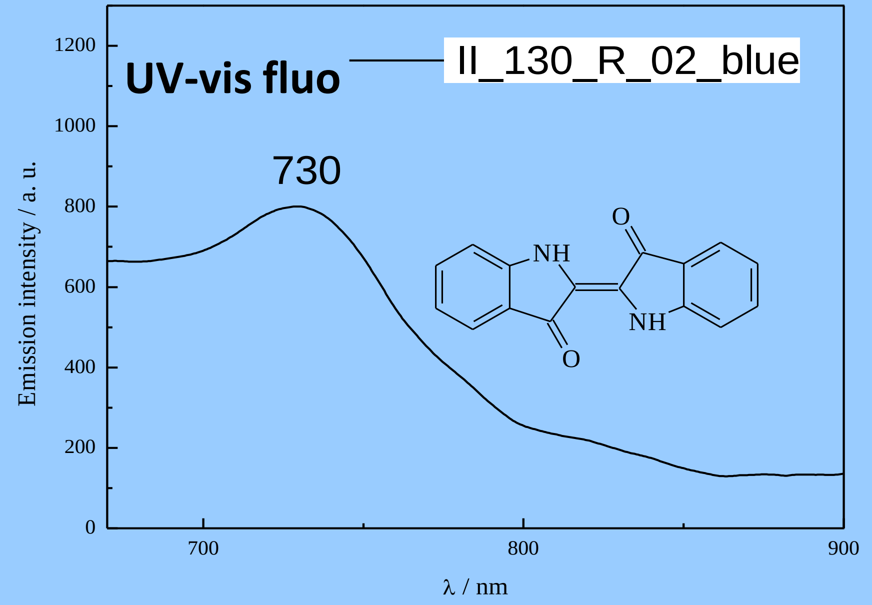
Blue

XRF: Pb, Ca, (S, K, Fe)

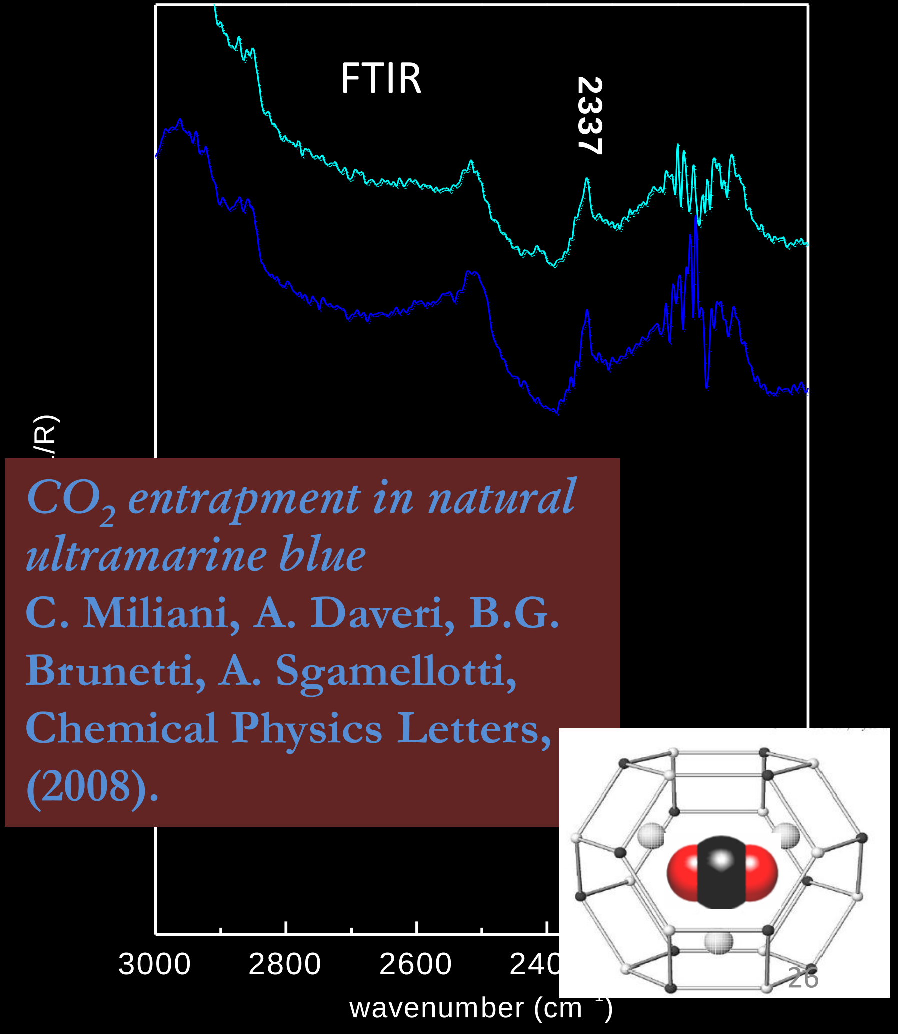
FTIR: lead white and 2337 cm^{-1} (CO_2)

Raman: ultramarine

UV-vis fluo: indigo

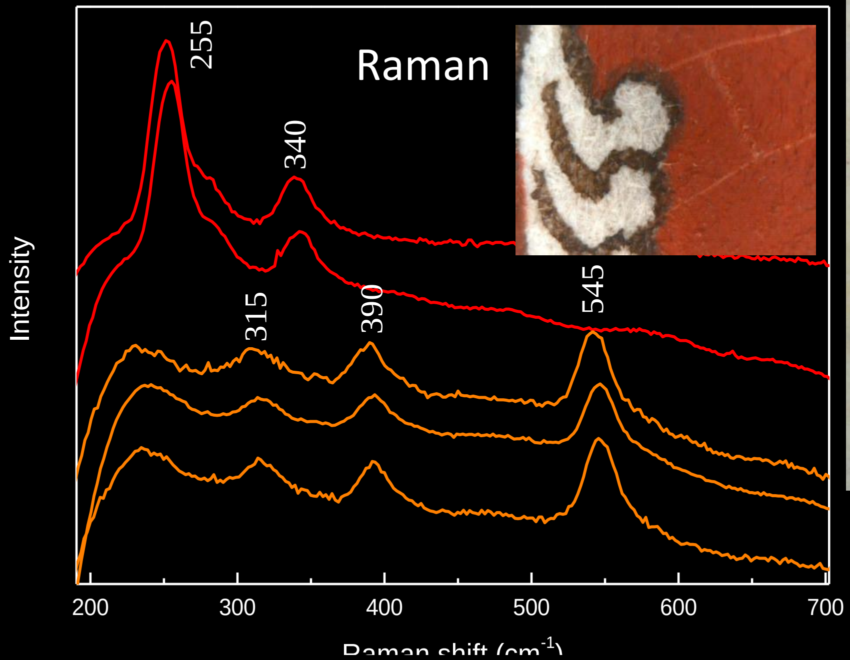


C. Miliani, A. Romani and G. Favaro, *Spectrochim. Acta* **Part A 54, (1998) 581-588.**



CO_2 entrapment in natural ultramarine blue

C. Miliani, A. Daveri, B.G. Brunetti, A. Sgamellotti, Chemical Physics Letters, (2008).

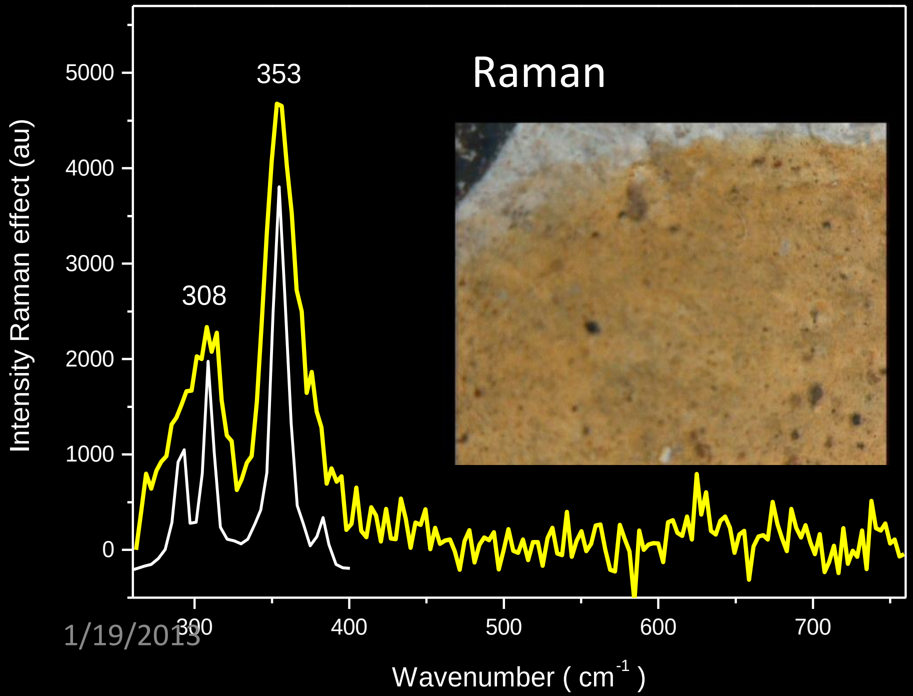


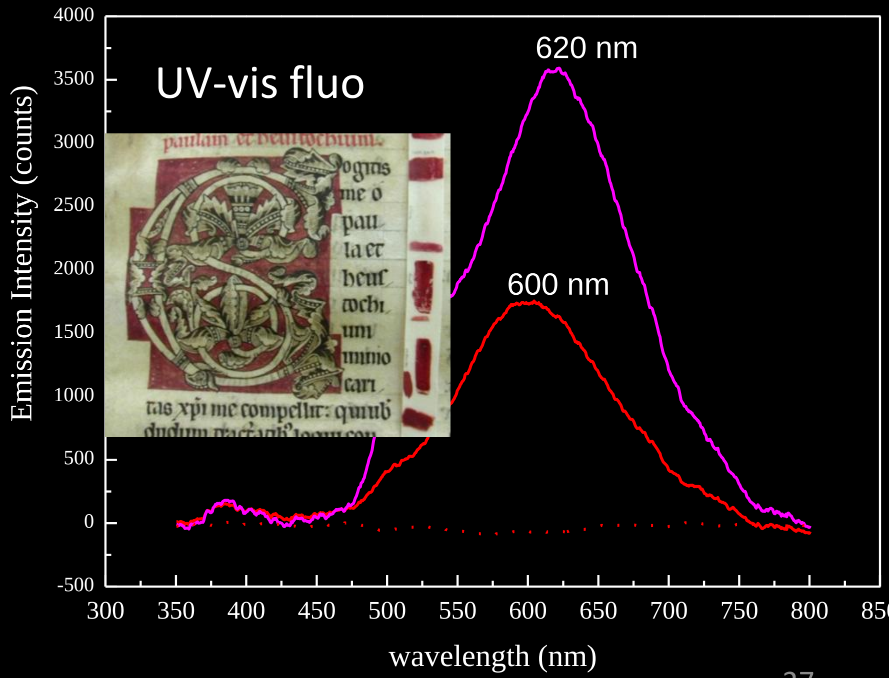
Red/Yellow/Purple

XRF: Hg, Ca, Pb, As…..

Raman: minium, cinnabar , orpiment

UV-vis fluo: red dyes





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6. Suppression of fluorescence: SERS

Study of pigment vibrational properties

Lab work

Research Article

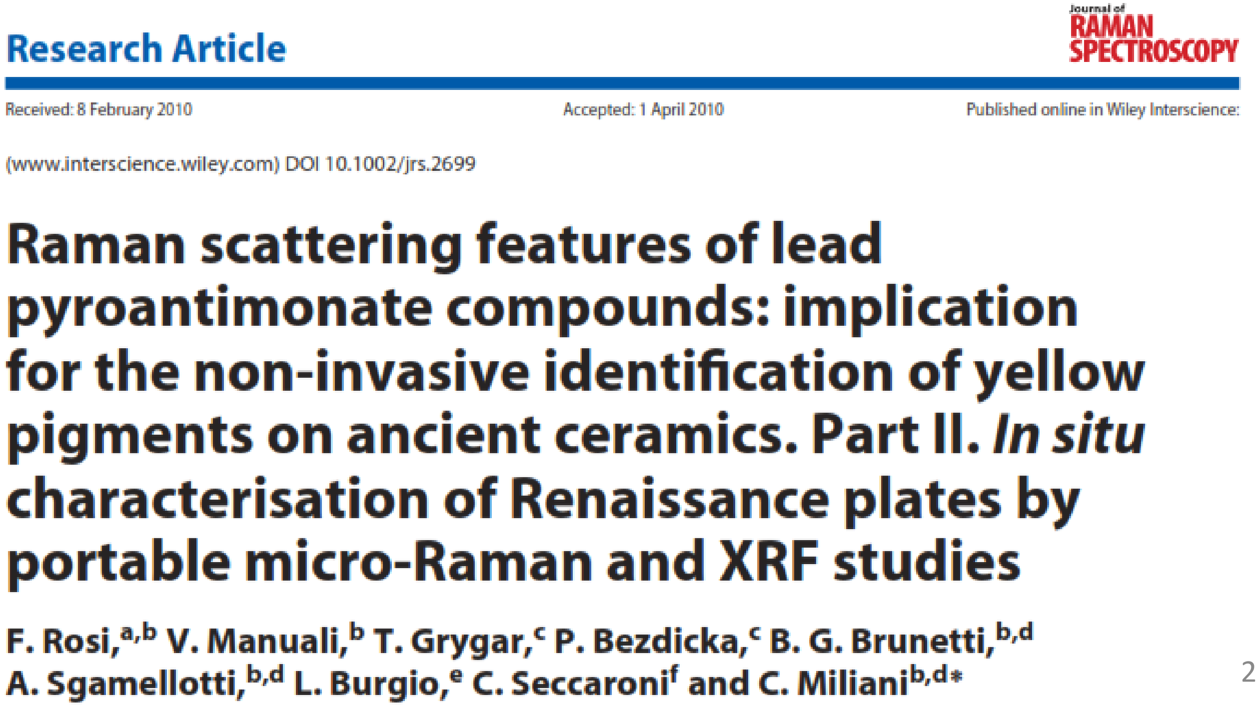
Journal of RAMAN SPECTROSCOPY

Received: 5 June 2008 Accepted: 17 July 2008

(www.interscience.com) DOI 10.1002/jrs.2092

Raman scattering features of lead pyroantimonate compounds. Part I: XRD and Raman characterization of $Pb_2Sb_2O_7$ doped with tin and zinc

F. Rosi,[a] V. Manuali,[a] C. Miliani,[a,b]* B. G. Brunetti,[a] A. Sgamellotti,[a,b]
T. Grygar[c] and D. Hradil[c,d]



Research Article

Journal of RAMAN SPECTROSCOPY

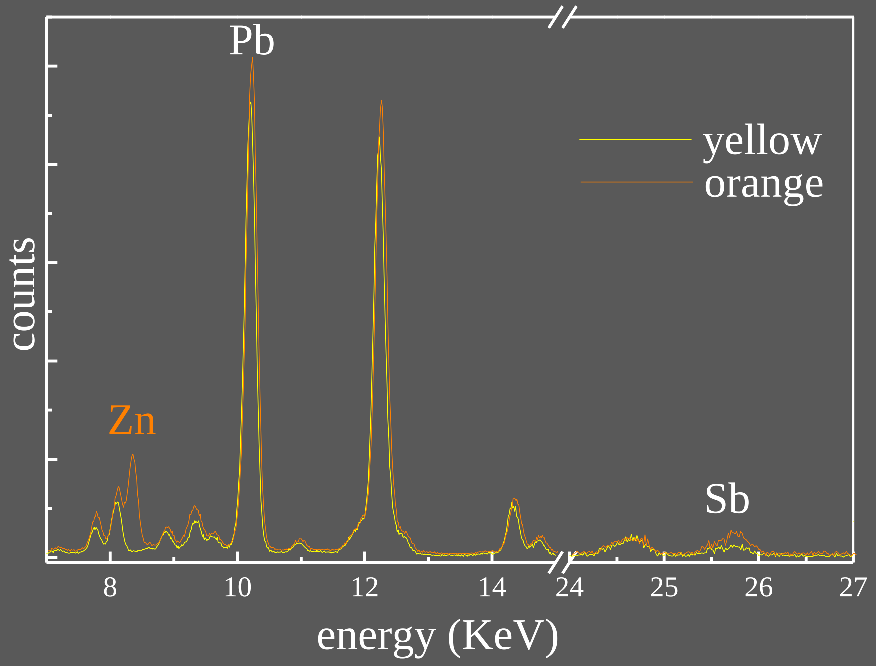
Received: 8 February 2010 Accepted: 1 April 2010

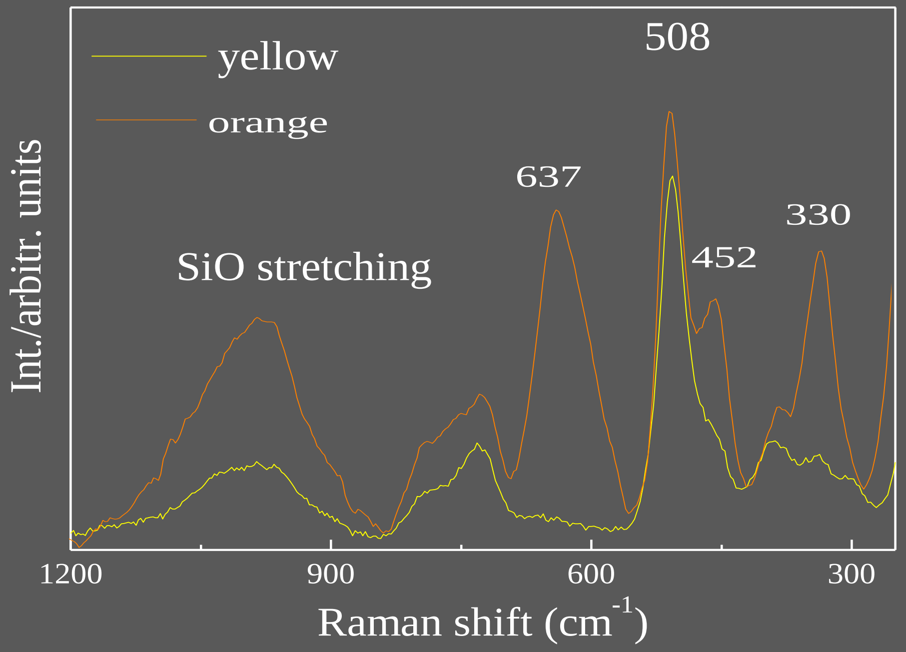
(www.interscience.wiley.com) DOI 10.1002/jrs.2699

Raman scattering features of lead pyroantimonate compounds: implication for the non-invasive identification of yellow pigments on ancient ceramics. Part II. *In situ* characterisation of Renaissance plates by portable micro-Raman and XRF studies

F. Rosi,[a,b] V. Manuali,[b] T. Grygar,[c] P. Bezdicka,[c] B. G. Brunetti,[b,d]
A. Sgamellotti,[b,d] L. Burgio,[e] C. Seccaroni[f] and C. Miliani[b,d]*

Renaissance lustrewares Museum collection of the V&A of London





C.Piccolpasso within *Li tre libri dell'arte del vasaio (1548)*

"…..Molti usano per fare il zalulino che sia in tutta bellezza, mettervi alquanto di tutia alessandrina*, che è molto ottima."

(*) The so-called "tuzia" is an impure Zn oxide left on the walls of ovens after the fusion of minerals containing Zn.

In spite of the available historical documentation only two cases have been reported in the literature (Seccaroni by XRF):

-a miniature by Valerio Mariani da Pesaro (~1580)
-a fragment of Renaissance pottery from central Italy (Casteldurante)

Naples yellow ($Pb_2Sb_2O_7$)

Naples yellow in ternary composition: Pb-Sb-Sn/Zn/Fe

Pb_3O_4, Sb_2O_3 in different Pb/Sb ratio NaCl flux, 900°C/10h

- **Pb_3O_4, Sb_2O_3 , SnO_2 NaCl, 900°C/10h**
- **$PbCO_3$, Sb_2S_3, SnO_2 NaCl, 900°C/10h**
- **Pb_3O_4, Sb_2O_3, ZnO NaCl, 900°C/10h**
- **Pb_3O_4, Sb_2O_3, Fe_2O_3 NaCl, 900°C/10h**

…from C.Piccolpasso: *Li tre libri dell'arte del vasaio, 1548*

XRD and UV-*vis* characterization of reaction products:

T. Grygar, D. Hradil,.. C. Miliani, at al. *J. Cult. Heritage*, **8** (2007) 377

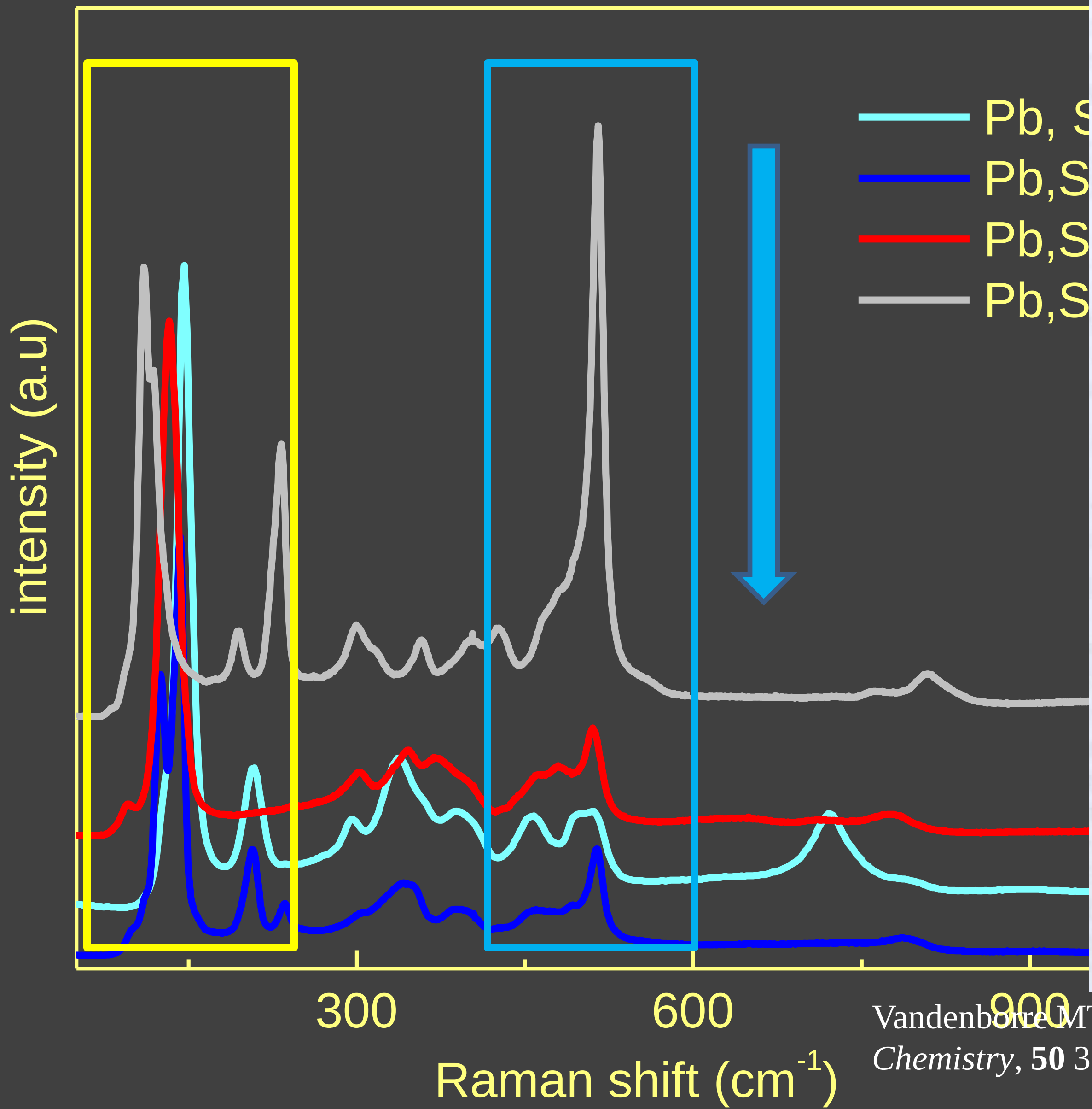
XRD and Rietveld analysis

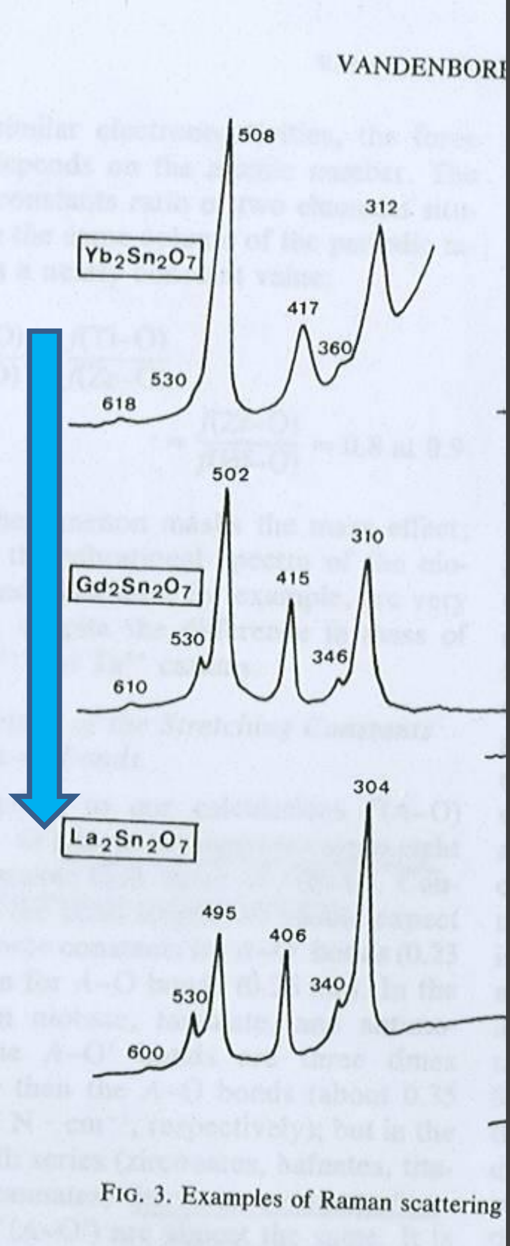
Sample	Reagent	Molar ratio	Lattice size of pyrochlore *a* (standard deviation in brackets) [Å]
PV_NY_25	Pb_3O_4, Sb_2O_3	**0.8:1 Pb:Sb**	**10.394 (0.002)**
PV_TY_1	Pb_3O_4, Sb_2O_3, SnO_2	**2:1.5:0.5 Pb:Sb:Sn**	**10.567 (0.004); 10.478 (0.004)**
PV_TY_60	$PbCO_3$, Sb_2S_3, SnO_2	**2.2:1.33:0.67 Pb:Sb:Sn**	**10.560 (0.002); 10.500 (0.002)**
PV_TY_11	Pb_3O_4, Sb_2O_3, ZnO	**2:1.5:0.5 Pb:Sb:Zn**	**10.496 (0.002)**

XRD data suggested that Sn and Zn are both entered in octahedral sites then causing deformation of the local symmetry of the ideal pyrochlore structure. The small expansion in the average cubic pyrochlore unit cell dimension can be interpreted on the basis of ionic size considerations, indeed the octahedral coordination cation radius increases in the order of $Sb^{5+} < Sn^{4+} < Zn^{2+}$.

The effect of the third atom on Raman

$I_{500}/I_{100}= B_2O_6/A_2O$



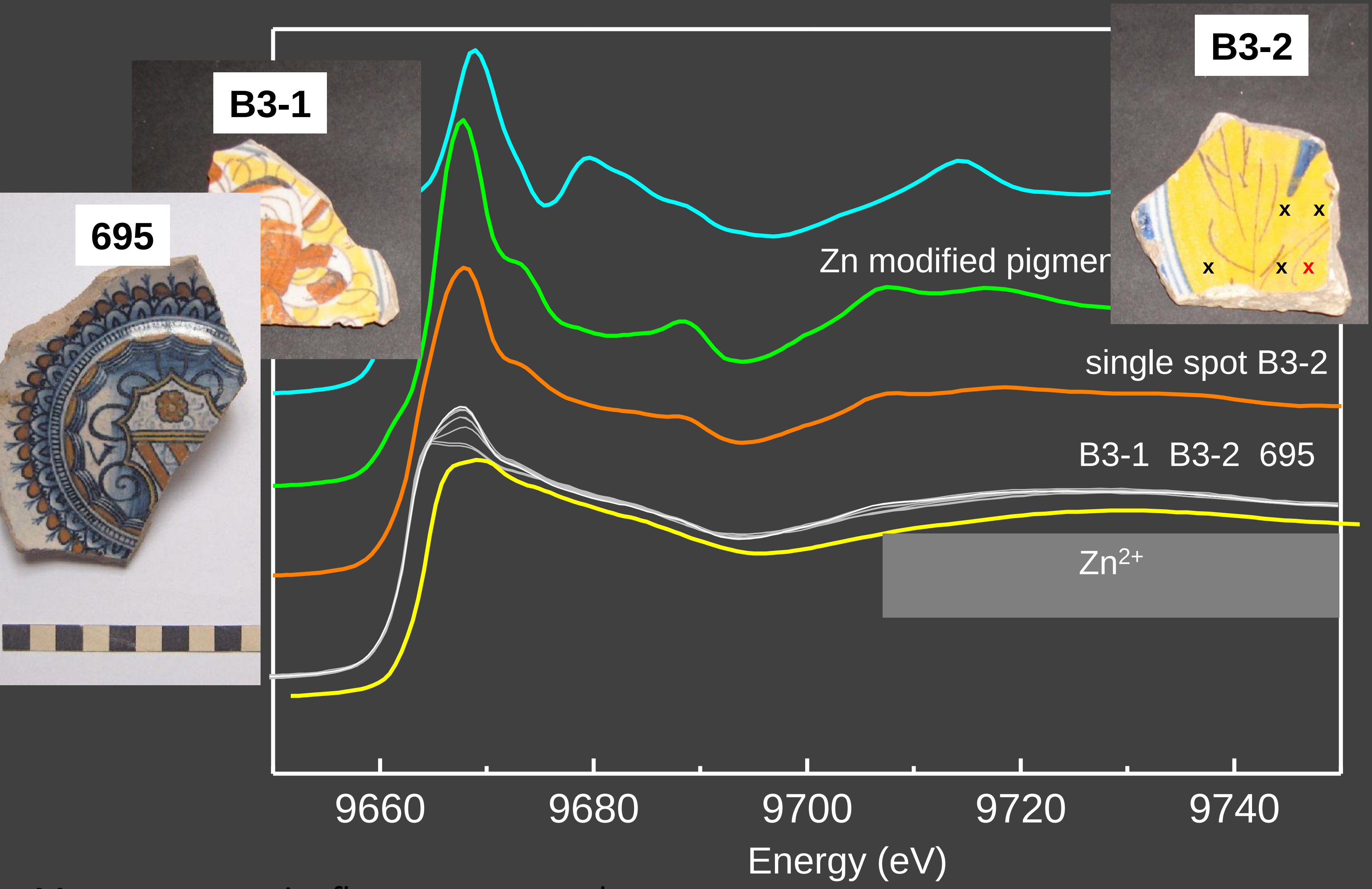


VANDENBORE

FIG. 3. Examples of Raman scattering

Vandenborre MT, Husson E, *Journal of Solid State Chemistry*, **50** 362 (1983)

XAS spectra at the Zn K-edge (9.659 keV)



L. Cartechini, D'Acapito, B.Brunetti et al. *J. Anal. At. Spectrom.* 26 (2011) 2500

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6. Suppression of fluorescence: SERS

Lab work

A Vibrational Study of Chrome Yellow Pigments ($PbCrO_4$, $PbCr_{1-x}S_xO_4$) and Their Detection on Paintings by Vincent van Gogh and Contemporaries

Letizia Monico

Antwerp University Perugia University - CNR-ISTM

Consiglio Nazionale delle Ricerche

CHARISMA

VAN GOGH MUSEUM AMSTERDAM

K. Janssens

C. Miliani

B. G. Brunetti

E. Hendriks

Monico, L. et al., submitted to *Anal. Chem.*

Introduction: chrome yellow alteration

Chrome yellow
($PbCrO_4$, $PbCrO_4 \cdot xPbO$, $PbCrO_4 \cdot xPbSO_4$)

- ➢ Synthetic pigment commonly used by artists of the 19th-20th C, such as V. van Gogh, P. Gauguin, P. Cézanne, G. Seurat, J.M.W. Turner, J. Constable, C. Pissarro, J. Ensor.
- ➢ low stability to photochemical processes and weathering.

This pigment tends to gradually acquire a darker aspect, causing the original bright yellow color to become brown.

Sunflowers, fourth version: yellow background, National Gallery, London, England

Sunflowers, repetition of the 4th version (yellow background), Van Gogh Museum, Amsterdam, the Netherlands.

Cr(VI) → Cr(III) ?

Reducing agents of Cr(VI)

- UV-Visible light, heat, contaminants;
- atmospheric gases, such as SO_2 and H_2S;
- soil constituents (e.g. amino, humic and fulvic acids) and Fe(II);
- sulfides and sulfates;
- organic matter;
- semiconductors particles in aqueous solutions;
- H_2O_2 in acidic aqueous solutions.

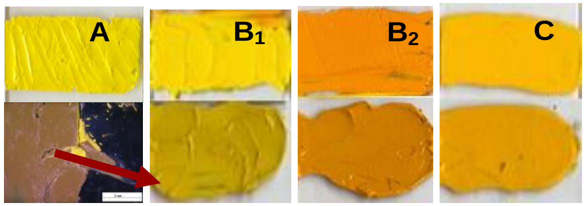
Model samples of lead chromate before and after ageing – Xe lamp, 800 h

19th historic oil paint tubes

R. Wouters (1882-1913)

Elsens, Bruxelles

$PbCrO_4$ + oil



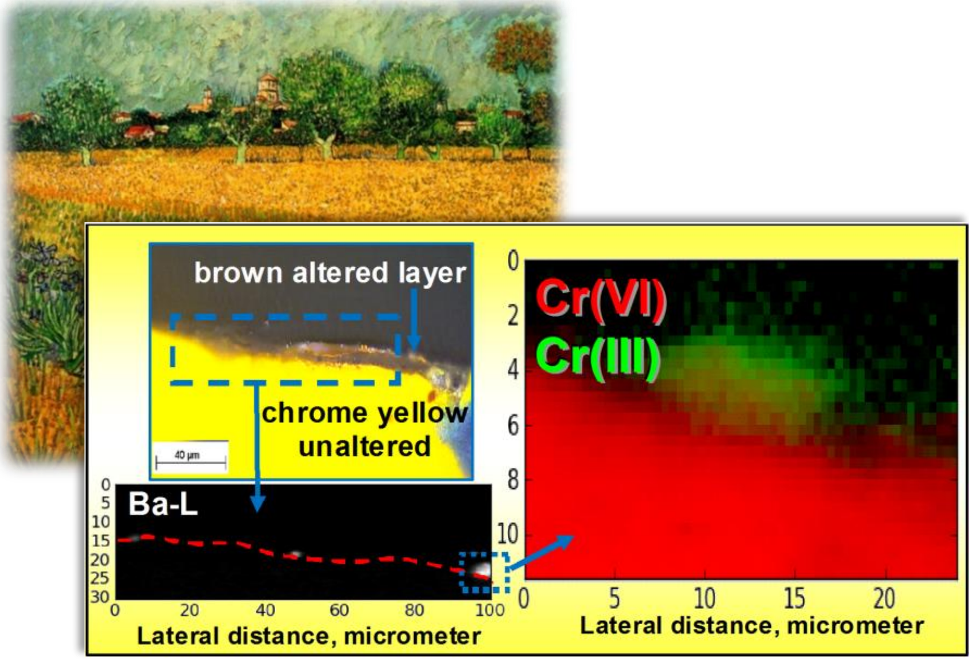
unaged

aged

Only the sample containing high amounts of sulfate showed a clear darkening [Cr(III) formation]

Embedded historic samples from paintings by Van Gogh (Van Gogh Museum, Amsterdam)

V. Van Gogh, View of Arles with Irises, 1888.

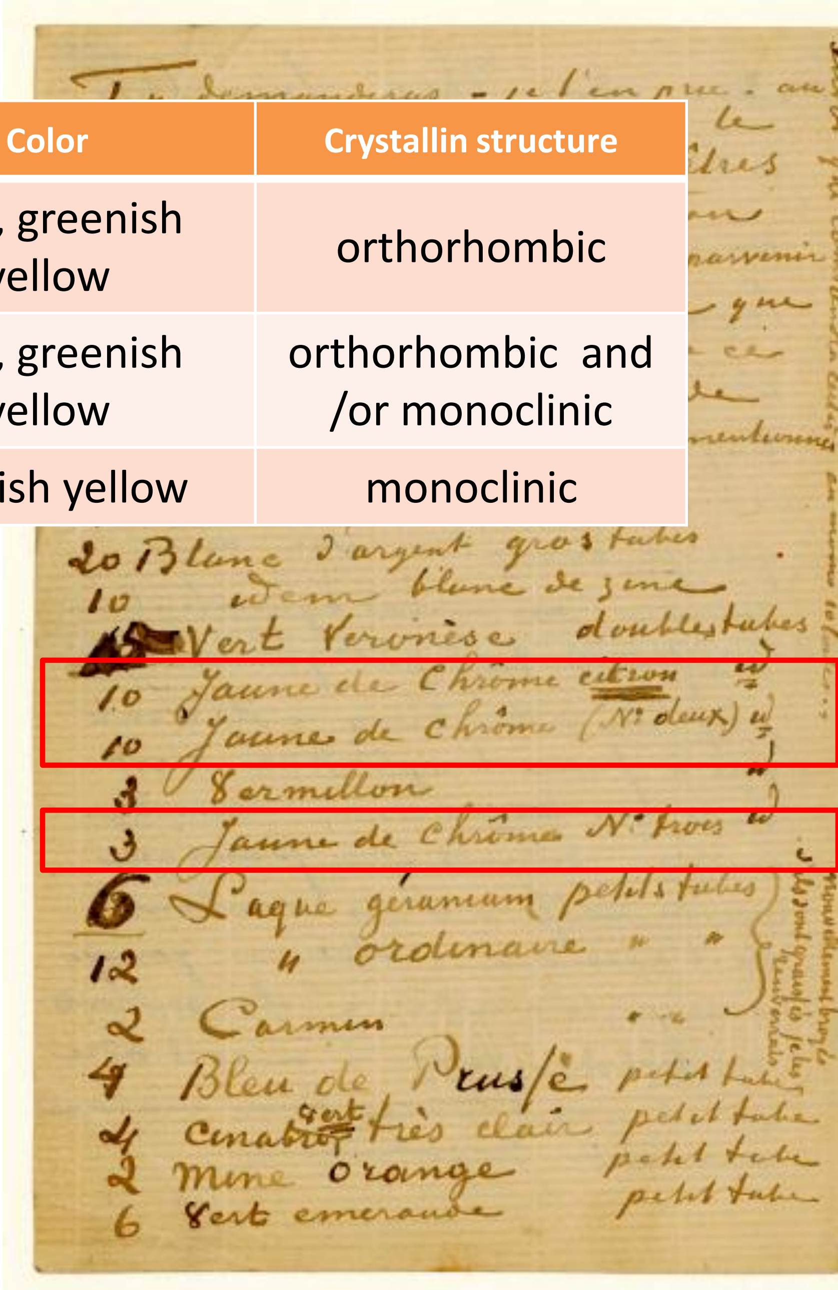


Detection of Cr(III) grains in the S-rich areas

- L. Monico, K. Janssens, C. Miliani et al., *Anal. Chem*. 83, 1214–1223 (2011).
- L. Monico, K. Janssens, C. Miliani et al., *Anal. Chem*. 83, 1224–1231 (2011).

Chrome yellow pigments: classification and chemical properties

Classification	Sulfate abundance (%)	Color	Crystallin structure
Primrose chrome	45-55	pale, greenish yellow	orthorhombic
Lemon chrome	20 -40	pale, greenish yellow	orthorhombic and /or monoclinic
Middle chrome	mainly pure $PbCrO_4$	reddish yellow	monoclinic



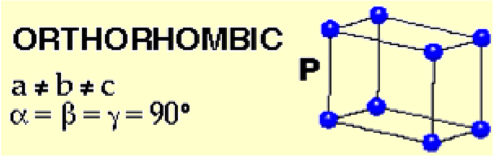
20 Blanc d'argent gros tubes
10 idem blanc de zinc
15 Vert Veronèse doubles tubes
10 Jaune de Chrôme citron id
10 Jaune de chrôme (N° deux) id
3 Vermillon id
3 Jaune de chrôme N° trois id
6 Laque géranium petits tubes
12 " ordinaire " "
2 Carmin " "
4 Bleu de Prusse petit tube
4 Cinabre vert très clair petit tube
2 Mine orange petit tube
6 Vert emeraude petit tube

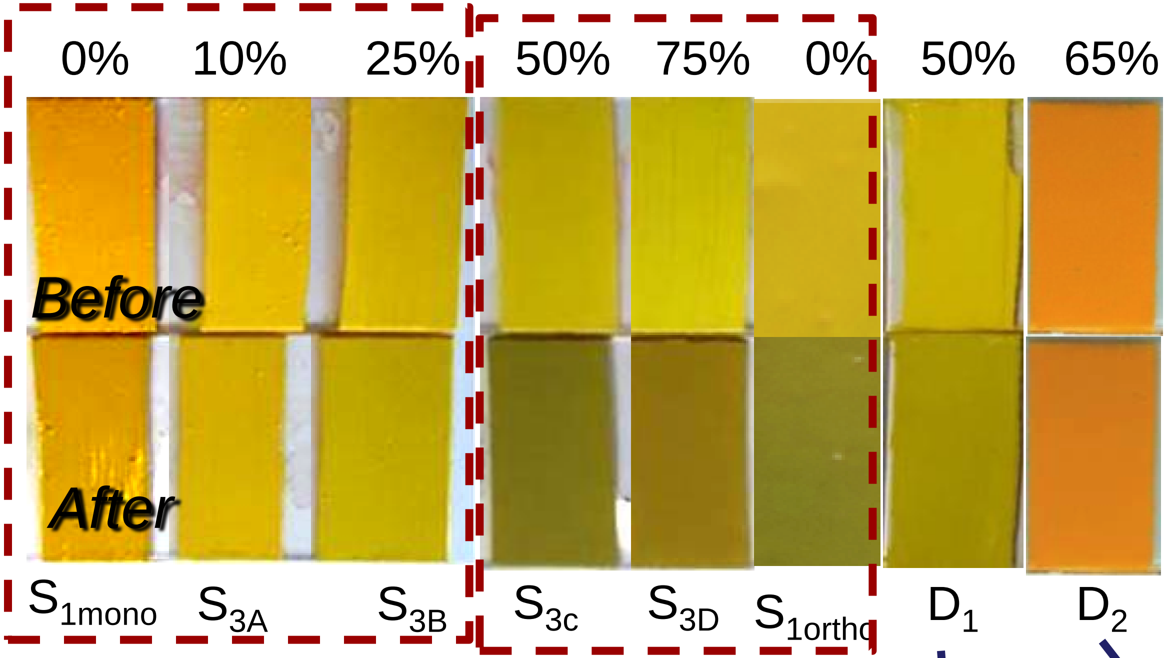
Van Gogh's letter to Theo, April 5th 1888

Ageing of model samples containing different $[SO_4^{2-}]$

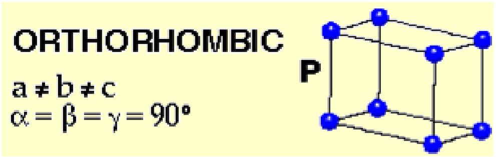
$[SO_4^{2-}]$

Orthorhombic phase, $SO_4^{2-} \geq 50\%$





Monoclinic phase, SO_4^{2-} ≤ 50%



Commercial powder
(CIBA, BASF)

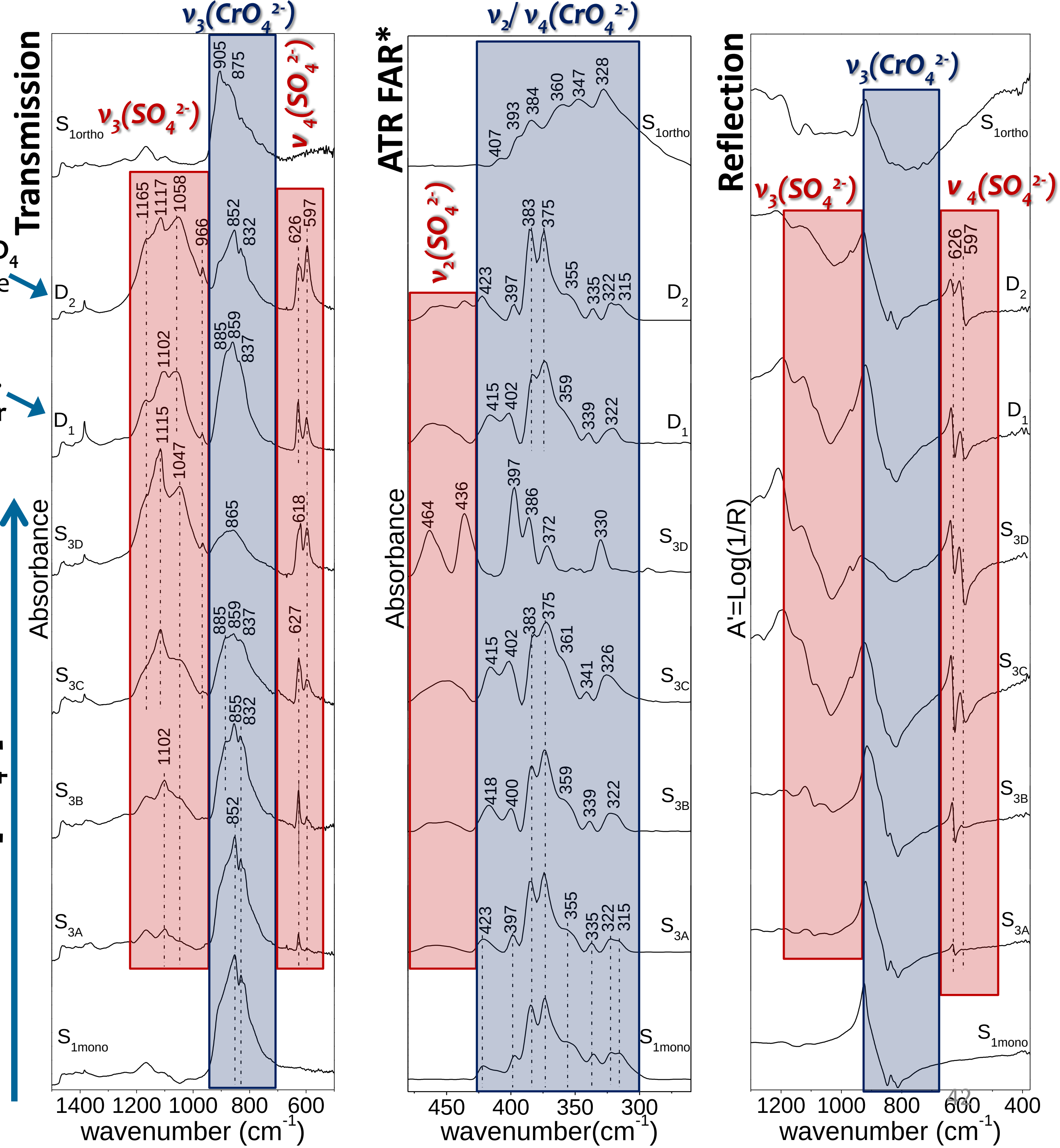
$PbCrO_4 + PbSO_4 (1:2)$

FTIR analysis

Lattice compression effect

Transmission/ ATR: progressive decreasing of the splitting signals (band broadening) and shift towards highest wavenumbers

Reflection:
spectral data distortions
- ➢ ν_3 $(SO_4^{2-})/(CrO_4^{2-})$: inverted by the *reststrahlen effect;*
- ➢ δ_4 (SO_4^{2-}): derivative-shape.

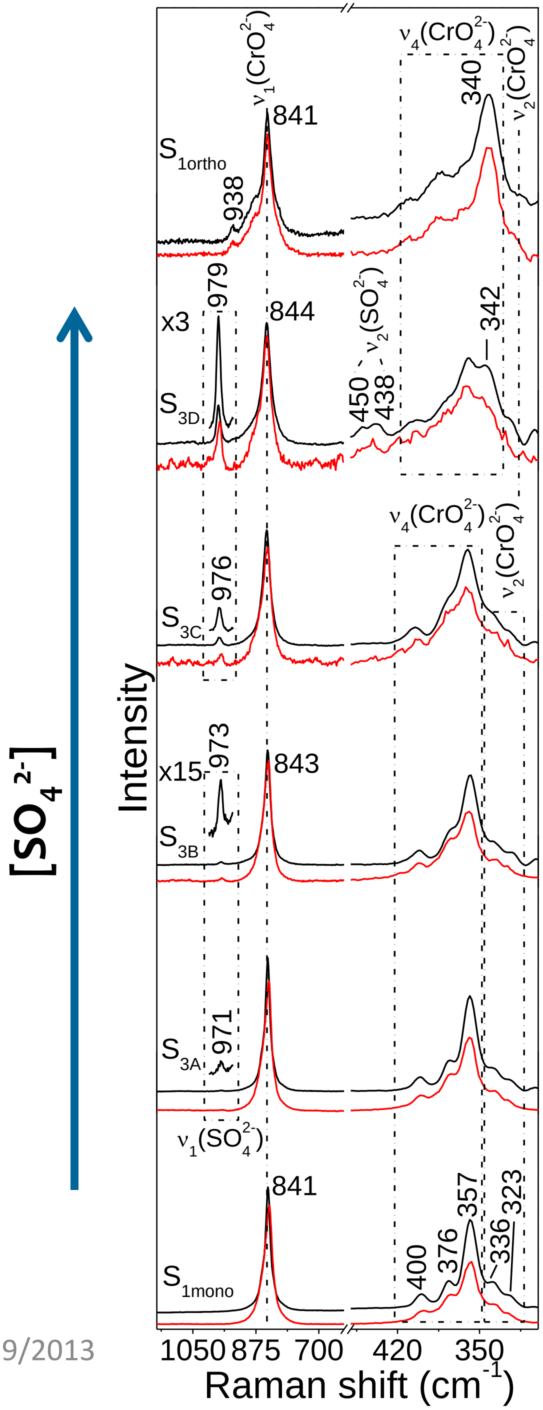


$PbCrO_4$ +$PbSO_4$ peaks of pure compounds

Comm. powder

*Analysis performed in collaboration with M. Cestelli Guidi - INFN (Frascati, Rome, IT)

μ-Raman analysis (exc. 785 nm)



When the sulfate amount increases:

1. the wavenumber of the $\nu_1(CrO_4^{2-})$ stretching mode, monotonically increases from 841 cm^{-1} for pure $PbCrO_4$ (S_{1mono}, S_{1ortho}) to 844 cm^{-1} for S_{3C} and S_{3D}. The half-width of this component also increases.

2. a progressive shift of the position towards highest energy, increase of the band half-width and a change of the relative intensities are observed also for the components describing the chromate bending modes (400-280 cm^{-1})

3. similar to the chromate vibrations, the $\nu_1(SO_4^{2-})$ position shifts from 971 cm^{-1} (S_{3A}) to 980 cm^{-1} (D_2, the pure $PbSO_4$)

benchtop *vs.* **portable**

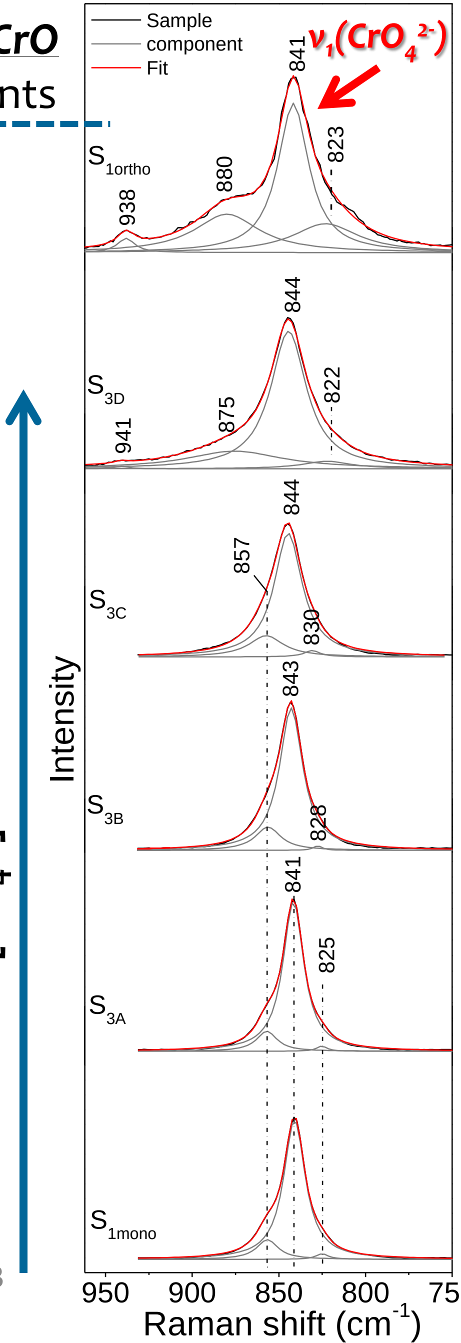
…..on paint models

μ-Raman analysis (exc. 785 nm)

Strerching CrO

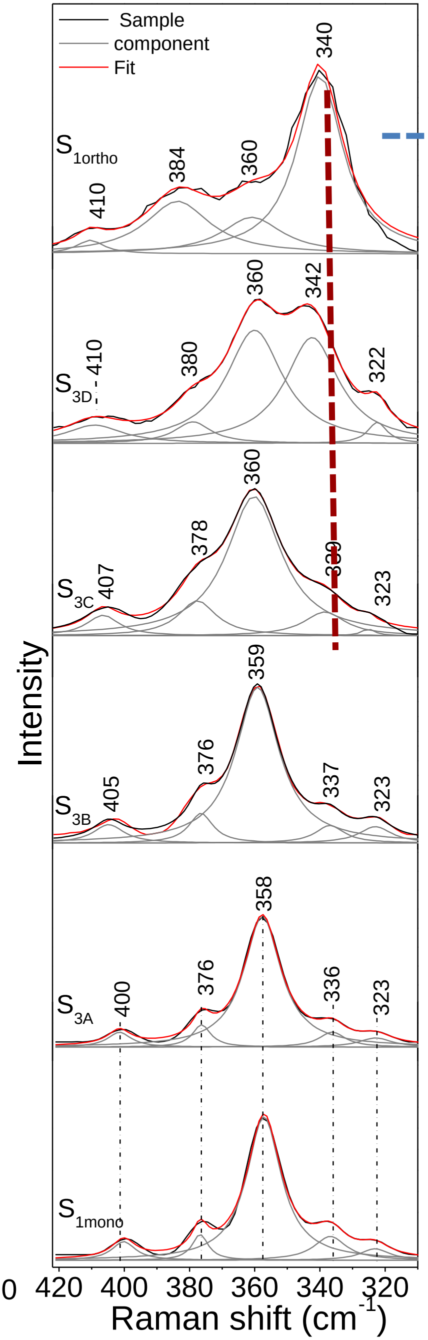
3 components

$[SO_4^{2-}]$



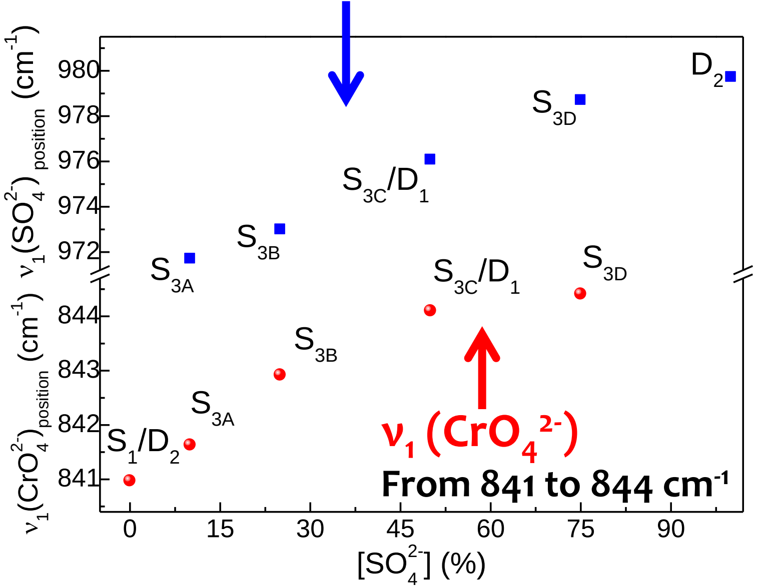
Bending CrO

5 components



$\nu_1 (SO_4^{2-})$

From 971 to 979 cm^{-1}



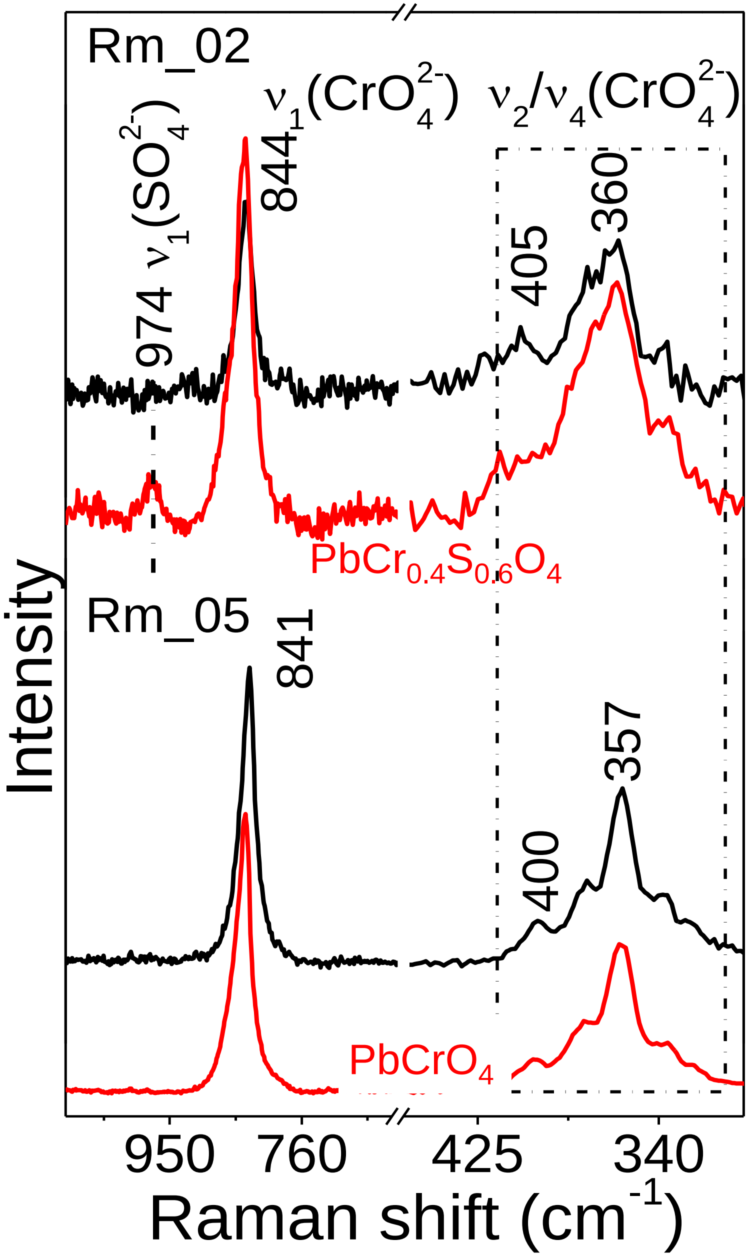
$\nu_1 (CrO_4^{2-})$

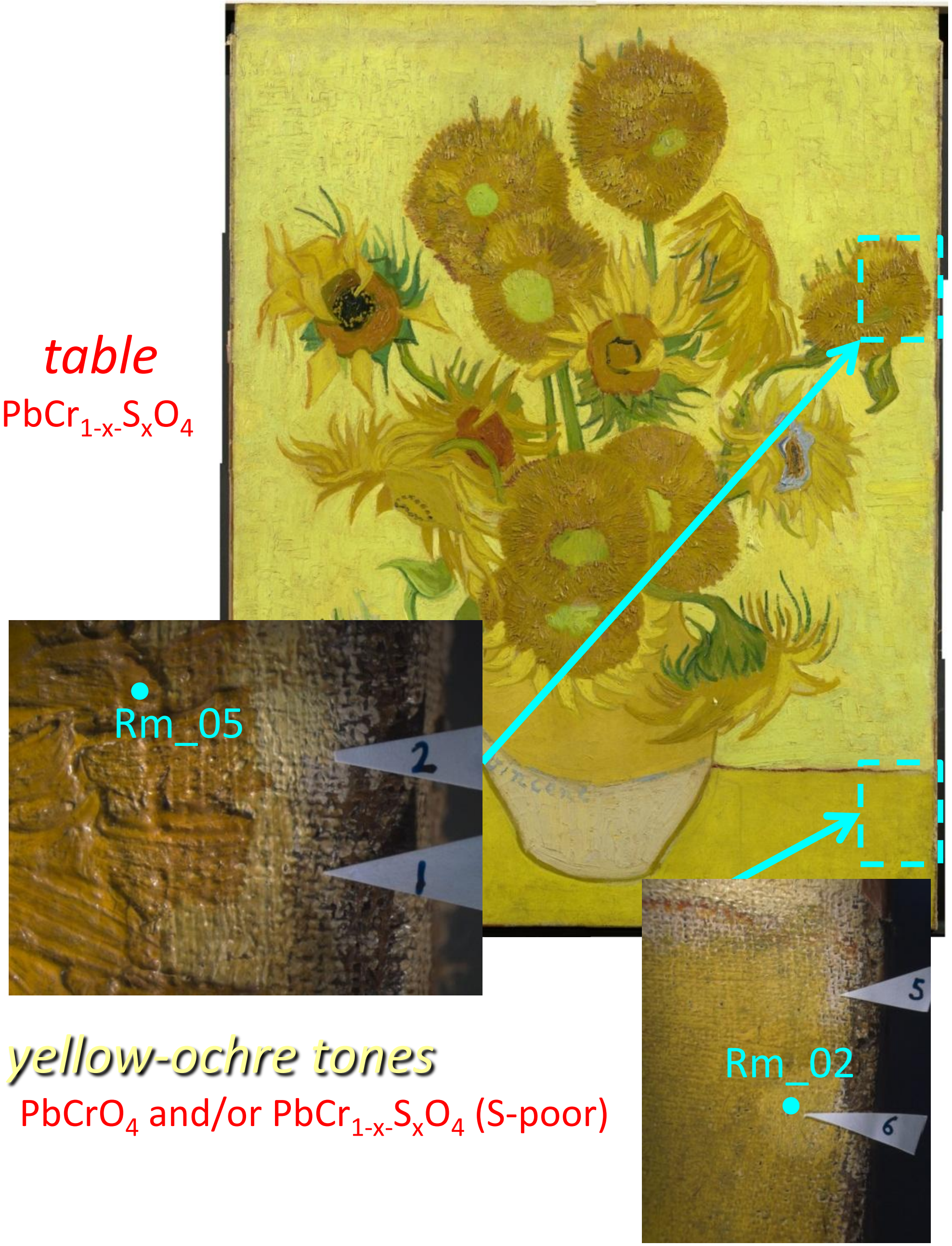
From 841 to 844 cm^{-1}

- When $[SO_4^{2-}]$ is increased:
  - decreasing of the splitting signals;
  - shift towards highest energies.

- Crystalline phases → Influence of the band-shape

cleaned areas – Raman (785 nm, 8-10 mW)





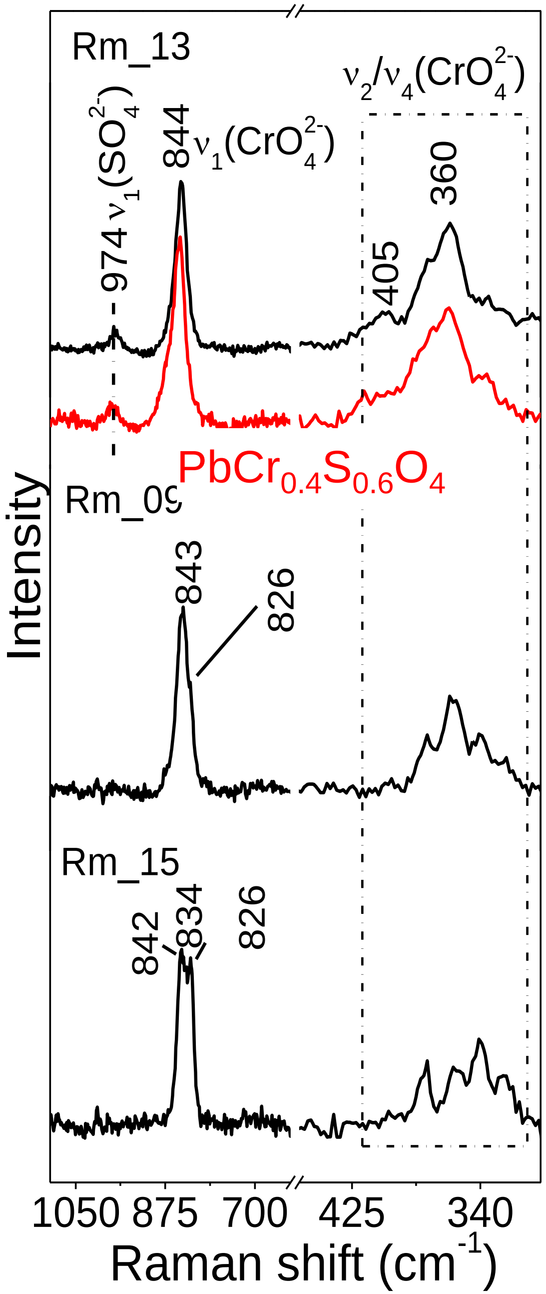
table

$PbCr_{1-x-}S_xO_4$

yellow-ochre tones

$PbCrO_4$ and/or $PbCr_{1-x-}S_xO_4$ (S-poor)

varnished regions – Raman (785 nm, 8-10 mW)



yellow tones

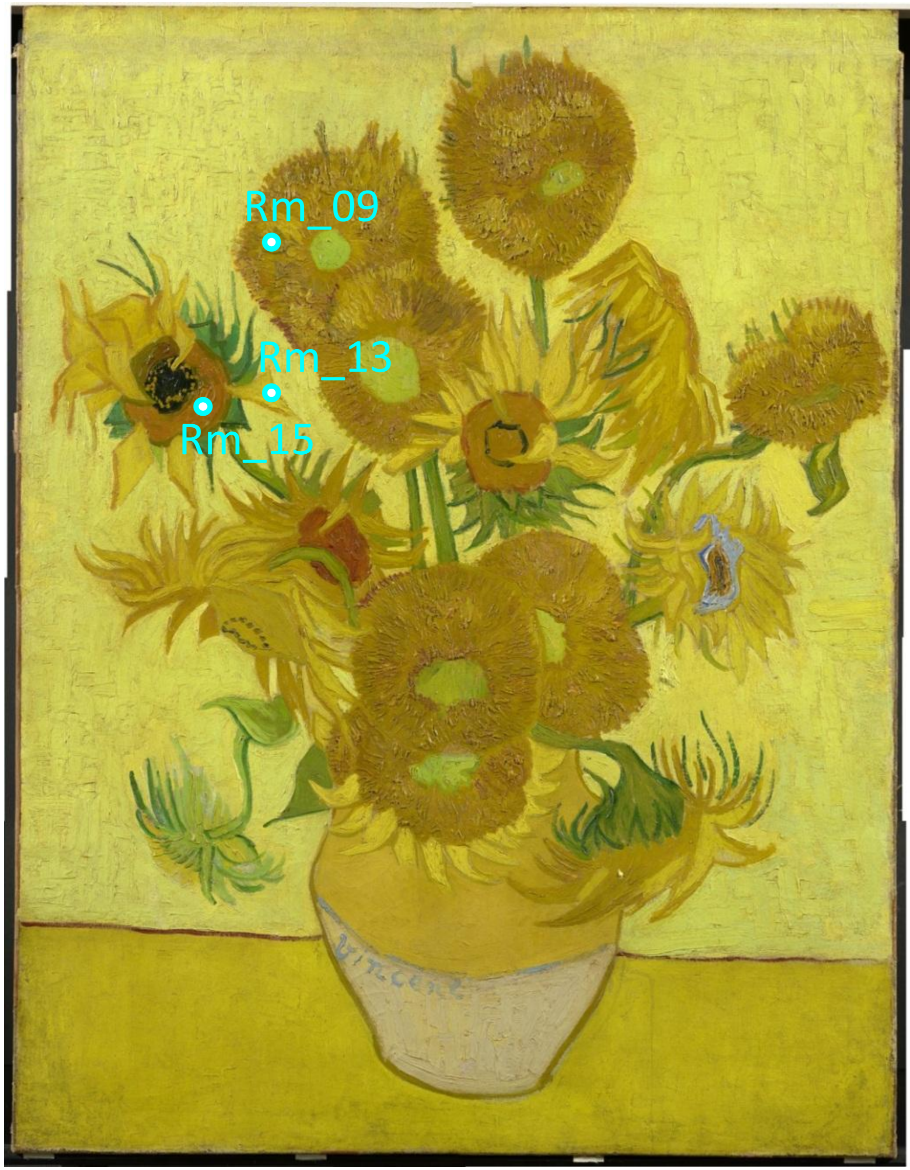
$PbCr_{1-x-}S_xO_4$

yellow-orange tones

$PbCr_{1-x-}S_xO_4$ and Chrome orange

orange tones

Chrome orange ($PbCrO_4 \cdot PbO$ – pheonichocroite)



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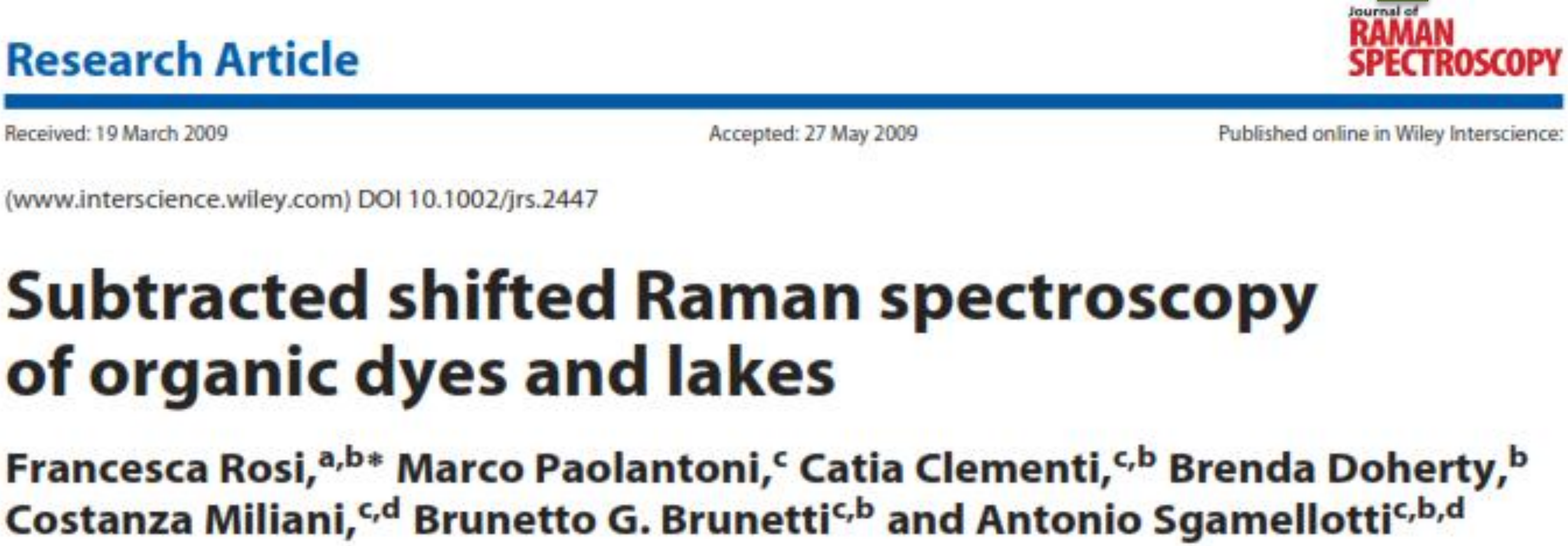
6. Suppression of fluorescence: SERS

Post processing of spectra

Data
processing
&
managing



Research Article

Journal of RAMAN SPECTROSCOPY

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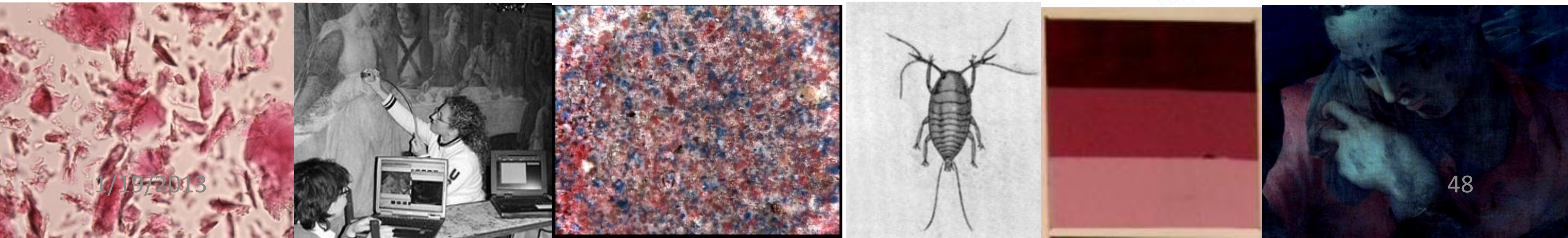
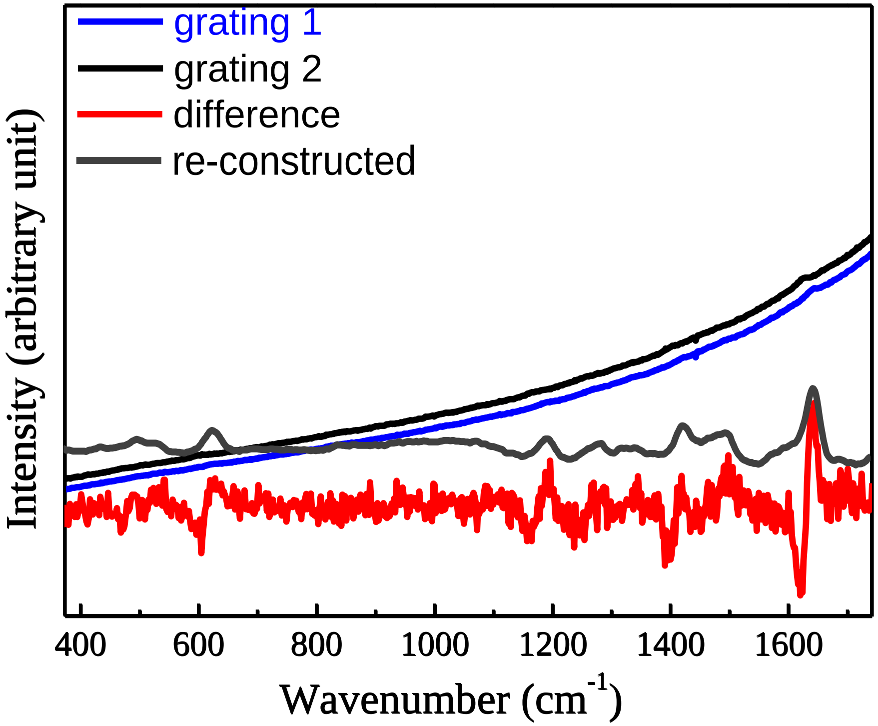
(www.interscience.wiley.com) DOI 10.1002/jrs.2447

Subtracted shifted Raman spectroscopy of organic dyes and lakes

Francesca Rosi,[a,b*] Marco Paolantoni,[c] Catia Clementi,[c,b] Brenda Doherty,[b]
Costanza Miliani,[c,d] Brunetto G. Brunetti[c,b] and Antonio Sgamellotti[c,b,d]

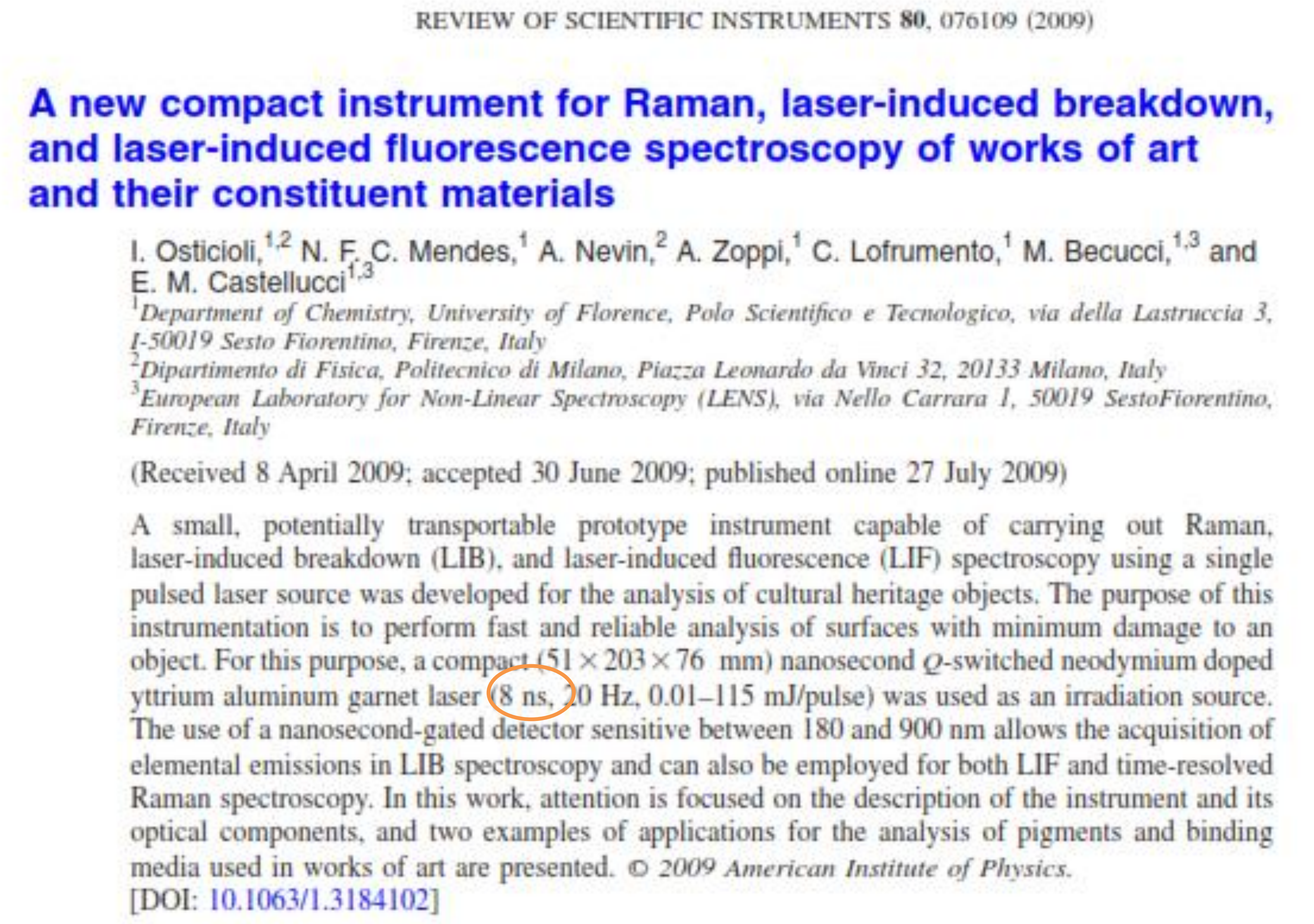


Subtracted Shifted Raman Spectroscopy



1. Raman spectra are recorded at two slight different grating positions
2. Subtraction of the two spectra gives a derivative-like spectrum from which the background has been eliminated.
3. Spectrum reconstruction

1. *P.A.Mosier-Boss et al. Applied Spectroscopy, 49, 630 (1995*)
2. *Identification of Dyes on Ancient Chinese Paper Samples Using the Subtracted Shifted Raman Spectroscopy Method, S. E. J. Bell et al. Anal. Chem. 2000, 72, 234-239*
3. *Fluorescence and Raman spectra on painting materials reconstruction of spectra with mathematical methods I.Osticioli et al. J.Raman Spectr. 2006, 37 974.*
4. *Subtracted shifted Raman spectroscopy of organic dyes and lakes Francesca Rosi et al. J.Raman Spectr 2010 41, 452.*



REVIEW OF SCIENTIFIC INSTRUMENTS **80**, 076109 (2009)

A new compact instrument for Raman, laser-induced breakdown, and laser-induced fluorescence spectroscopy of works of art and their constituent materials

I. Osticioli,[1,2] N. F. C. Mendes,[1] A. Nevin,[2] A. Zoppi,[1] C. Lofrumento,[1] M. Becucci,[1,3] and E. M. Castellucci[1,3]

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A small, potentially transportable prototype instrument capable of carrying out Raman, laser-induced breakdown (LIB), and laser-induced fluorescence (LIF) spectroscopy using a single pulsed laser source was developed for the analysis of cultural heritage objects. The purpose of this instrumentation is to perform fast and reliable analysis of surfaces with minimum damage to an object. For this purpose, a compact ($51\times203\times76$ mm) nanosecond *Q*-switched neodymium doped yttrium aluminum garnet laser (8 ns, 20 Hz, 0.01–115 mJ/pulse) was used as an irradiation source. The use of a nanosecond-gated detector sensitive between 180 and 900 nm allows the acquisition of elemental emissions in LIB spectroscopy and can also be employed for both LIF and time-resolved Raman spectroscopy. In this work, attention is focused on the description of the instrument and its optical components, and two examples of applications for the analysis of pigments and binding media used in works of art are presented. © *2009 American Institute of Physics.*

[DOI: 10.1063/1.3184102]

But…..luminescence time of decay of painting materials is quite short: 5-0.1 ns

Outline

1. Motivations and the context: the MOLAB

2. Portable equipment: issues and limitations

3. Identification of pigments: Raman & other techniques

4. Lead antimoniate yellows: $Pb_2Sb_{2-x}\,Y_xO_{7-x/2}$

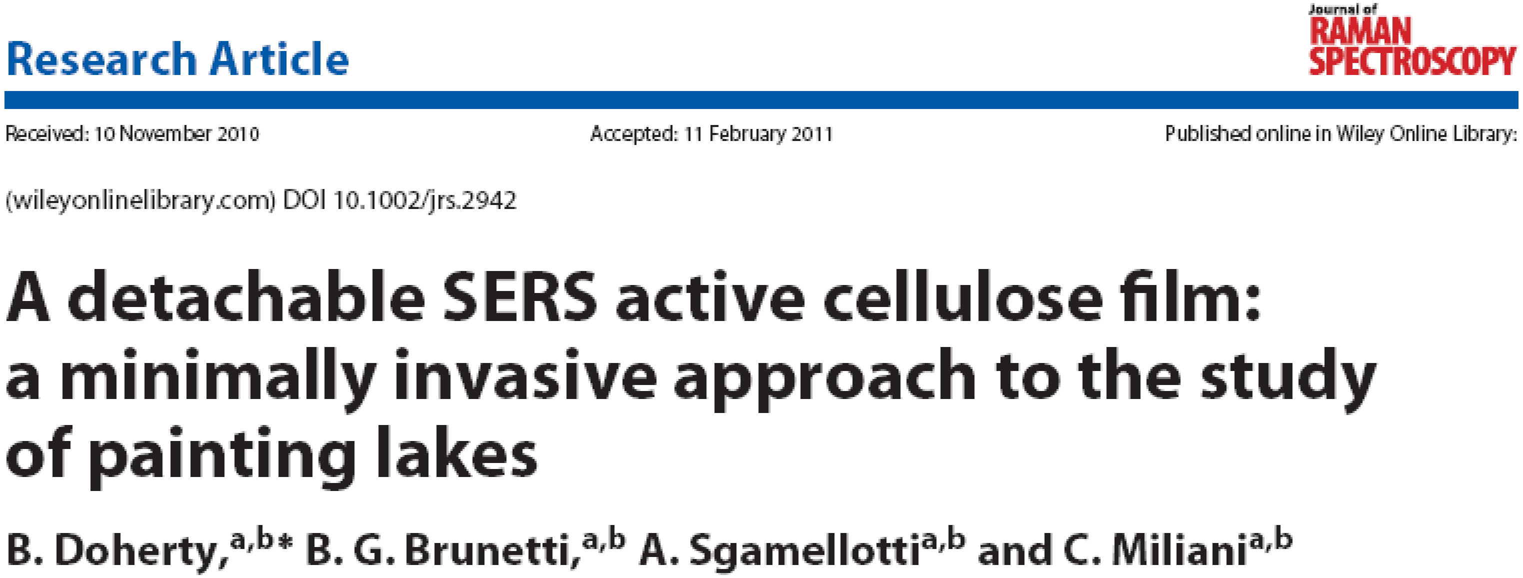
5. Chrome yellows: $PbCrO_4$, $PbCrO_4 \cdot xPbO$, $PbCrO_4 \cdot xPbSO_4$

6. Suppression of fluorescence: SSRS

7. Suppression of fluorescence: SERS

Developing new spectroscopic methods for non invasive analysis

Lab work



Research Article

Journal of RAMAN SPECTROSCOPY

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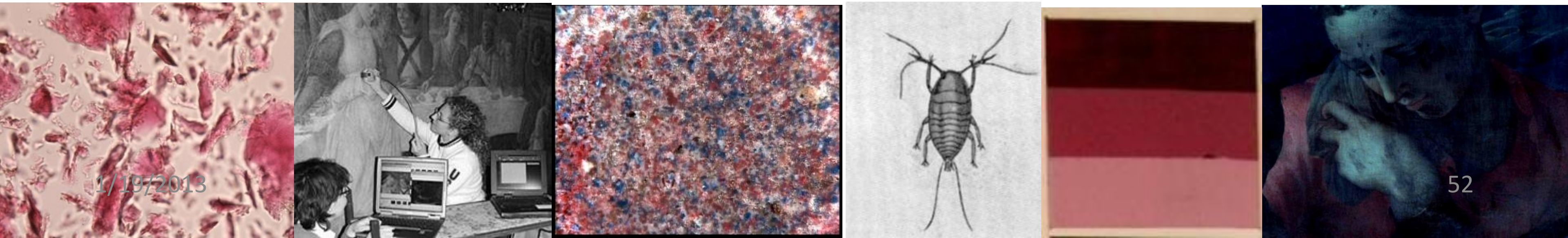
(wileyonlinelibrary.com) DOI 10.1002/jrs.2942

A detachable SERS active cellulose film: a minimally invasive approach to the study of painting lakes

B. Doherty,[a,b]* B. G. Brunetti,[a,b] A. Sgamellotti[a,b] and C. Miliani[a,b]

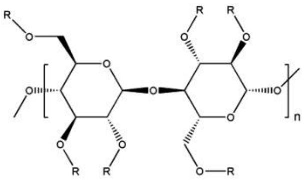


In situ non-invasive SERS measurements ?

A transparent **water soluble polymer doped with the AgNPs** has been specifically designed:

1. **Suitable average SERS enhancement**
2. **Good stability and reproducibility**
3. **Neutral pH**
4. **Transparency**
5. **Removability**

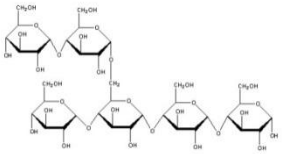
Methylcellulose



Cellulose: R = H
Methyl cellulose: R = CH_3 (40-90%) or H

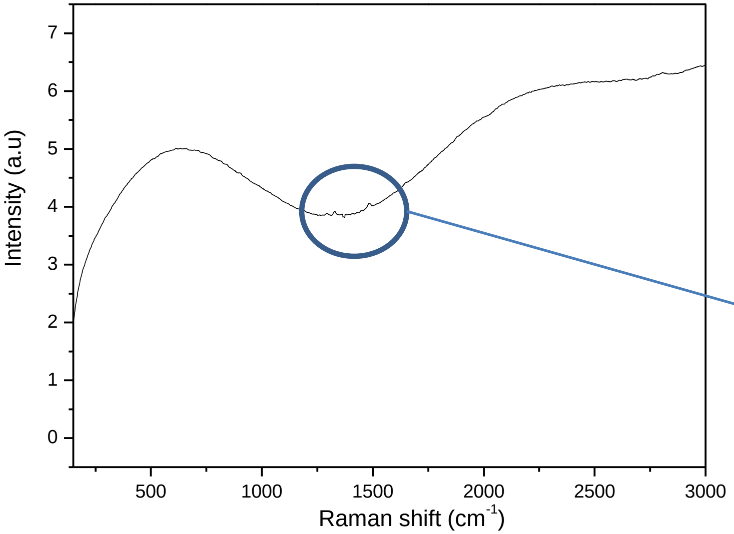
&

AgNP starch colloid

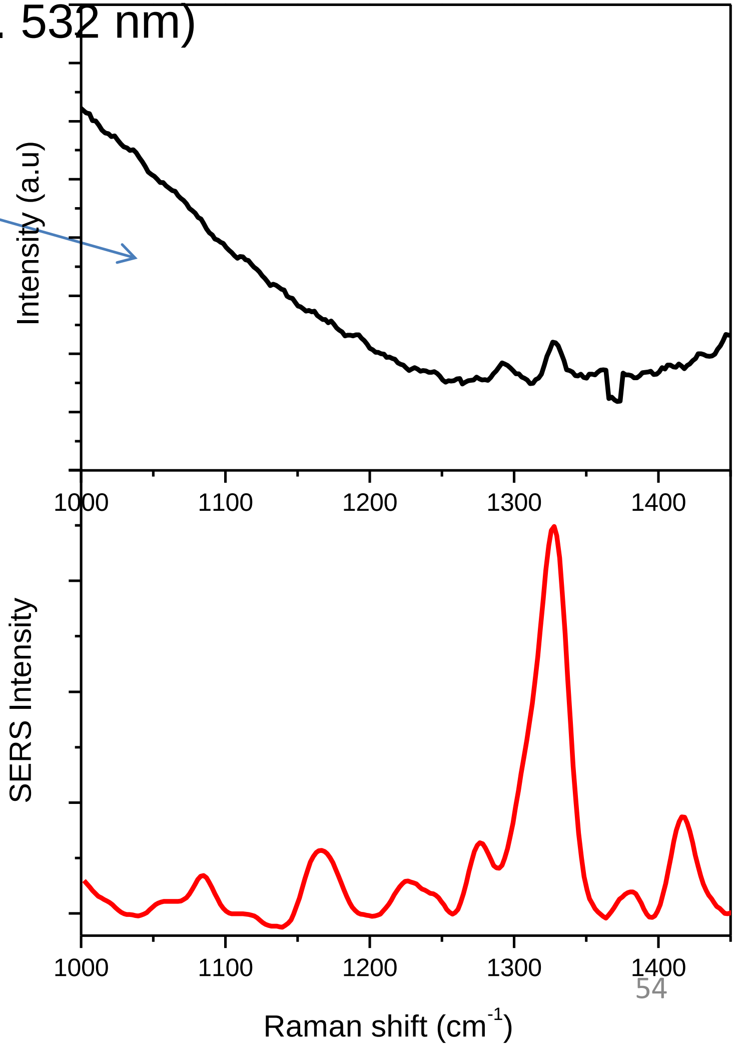


It is shown that silver nanoparticles prepared by green chemical reduction can be effectively doped into a methylcellulose matrix for the formation of a gel that can be applied to a minute area of an artwork to be studied and that after SERS measurements can be safely removed.

Study of madder lake painting models



Conventional Raman spectrum collected from the surface of mock-up made by madder lake and linseed oil (exc. 532 nm)

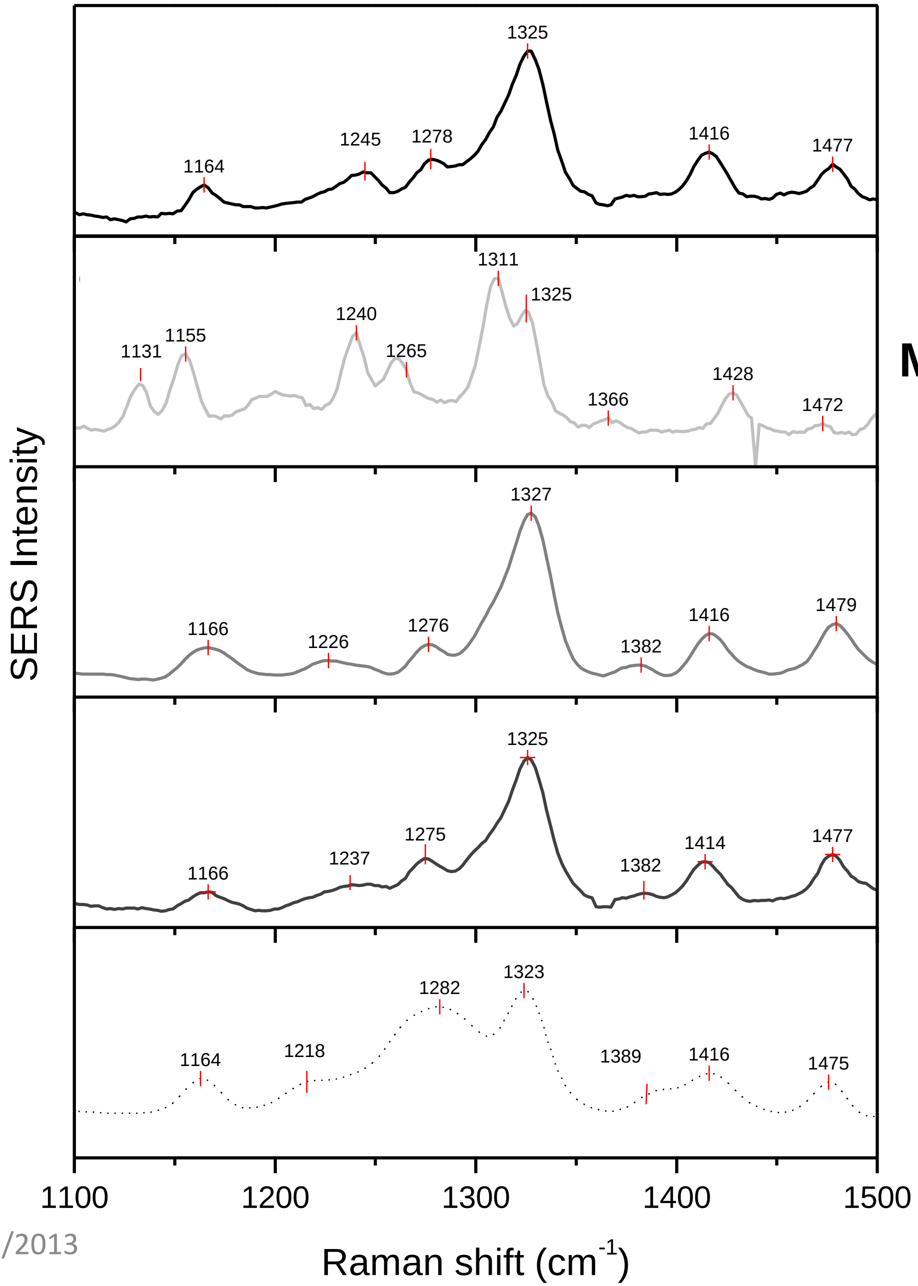


Qualitative Enhancement Factor (EF) of roughly **10^3 -10^4** , given by:

EF = I_{SER}/I_{RS} (@ 1325 cm^{-1})

SER spectrum collected from the surface of mock-up made by madder lake and linseed oil (exc. 532 nm)

Study of madder lake painting models



Madder & Casein

Madder & Wax (encaustic)

Madder & Linseed oil

Madder & Egg tempera

Madder

Conclusion

1. Motivations and the context: the MOLAB **ON-SITE!**

2. Portable equipment: issues and limitations **……a lot of!**

3. Identification of pigments: Raman & **<u>other techniques</u>**

4. Lead antimoniate yellows: $Pb_2Sb_{2-x}Y_xO_{7-x/2}$

………..Let's go for good R. scatterers…..

5. Chrome yellows: $PbCrO_4$, $PbCrO_4 \cdot xPbO$, $PbCrO_4 \cdot xPbSO_4$

6. **<u>Suppression of fluorescence</u>**: SSRS

7. **<u>Suppression of fluorescence</u>**: SERS

Acknowledgments 1/2

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CNR-ISTM

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Alessia Daveri, CNR-ISTM

…..and all the MOLAB team :
"…a roving crew of
conservation scientists that travel around Europe…."

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CHARISMA
SEVENTH FRAMEWORK PROGRAMME

…..for the financial support

and to you, for your kind attention!

costanza.miliani@cnr.it

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Pick your wavelength: dispersive & FT Raman approaches to the analysis of art materials

Francesca Casadio

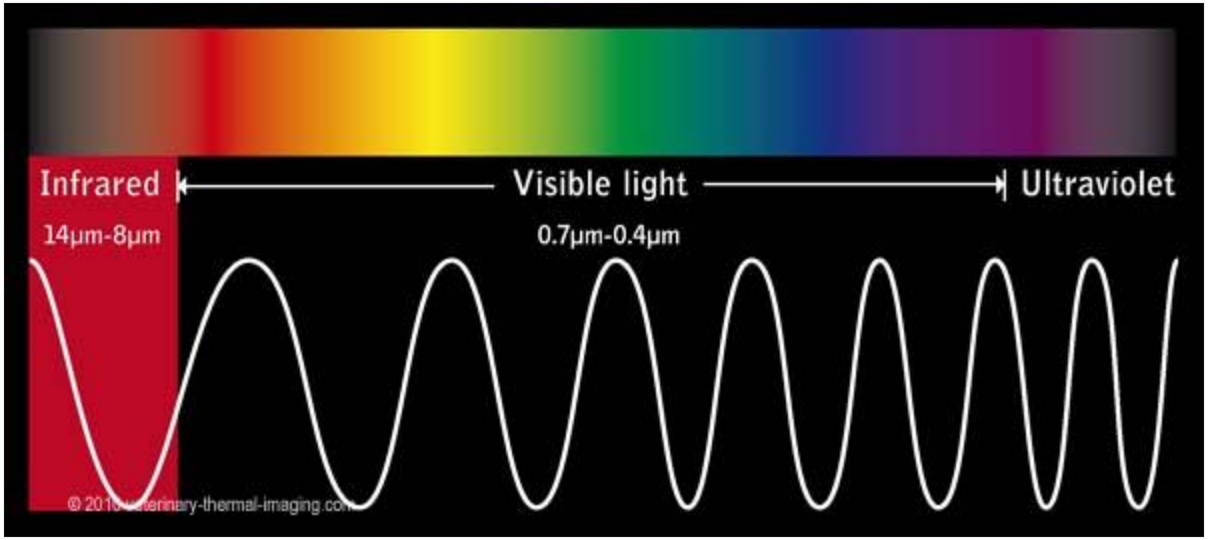
Art Institute of Chicago, US

FRIDAY, SEPTEMBER 28: LECTURE 8

ART
INSTITVTE
CHICAGO

Pick Your Wavelength:

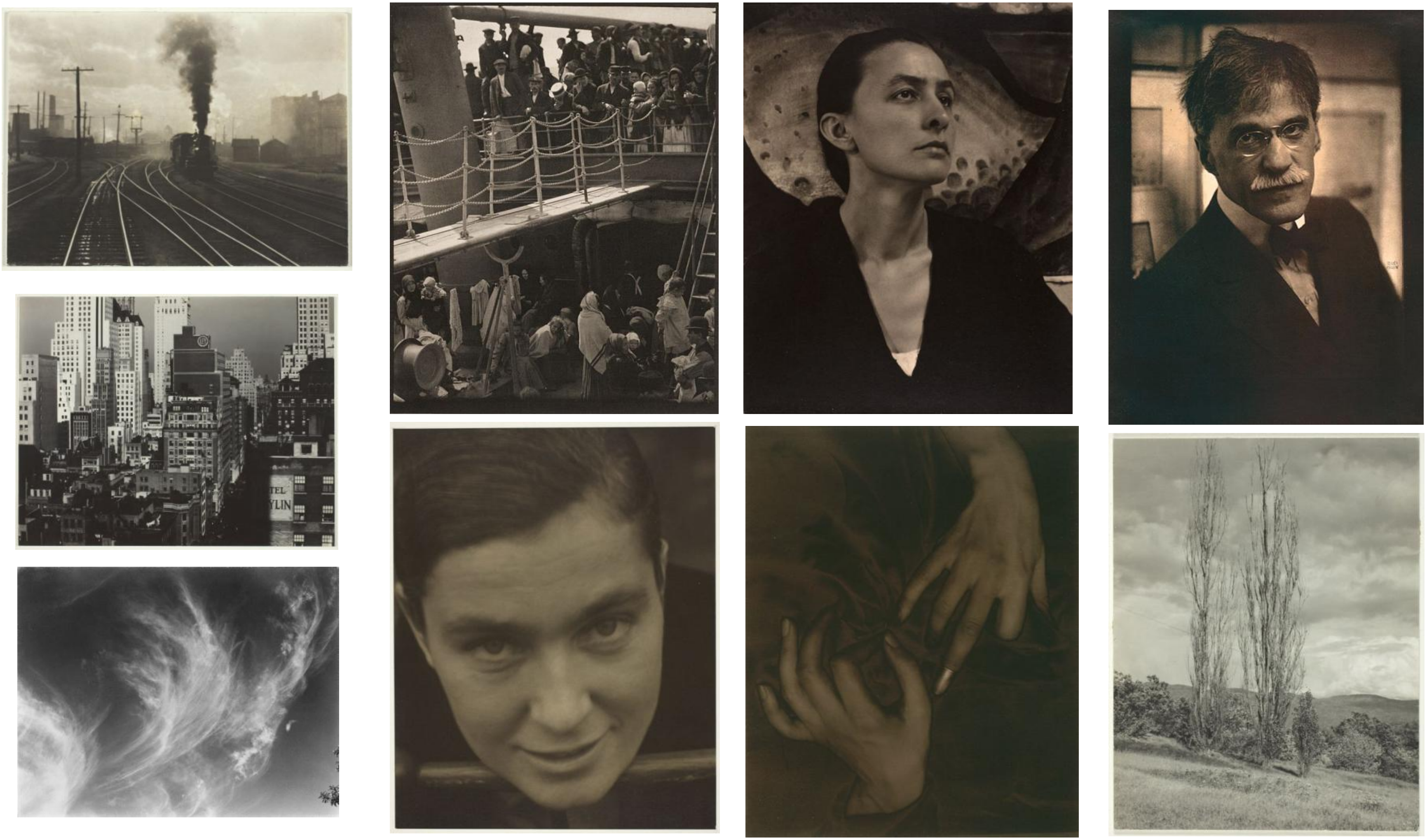
Dispersive & FT Raman Approaches to the Analysis of Art Materials



Francesca Casadio, Ph.D.
Andrew W. Mellon Senior Conservation Scientist,
The Art Institute of Chicago
fcasadio@artic.edu

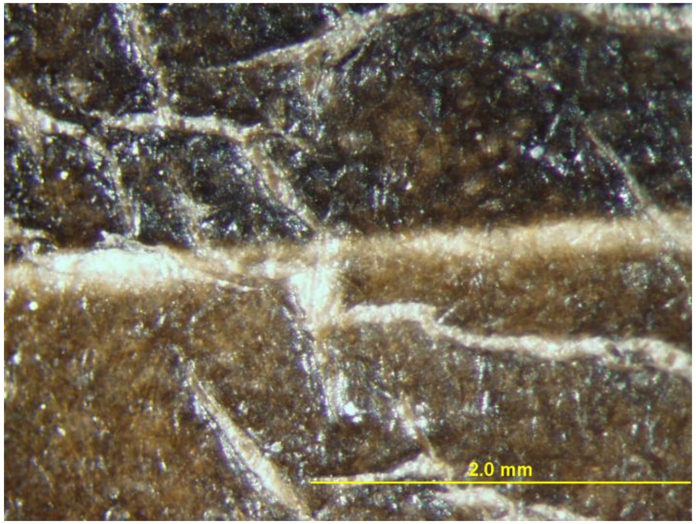
- Coatings on photographs
- Contemporary art materials
- Binding media
- Dyed paper fibers
- Colorants on paper

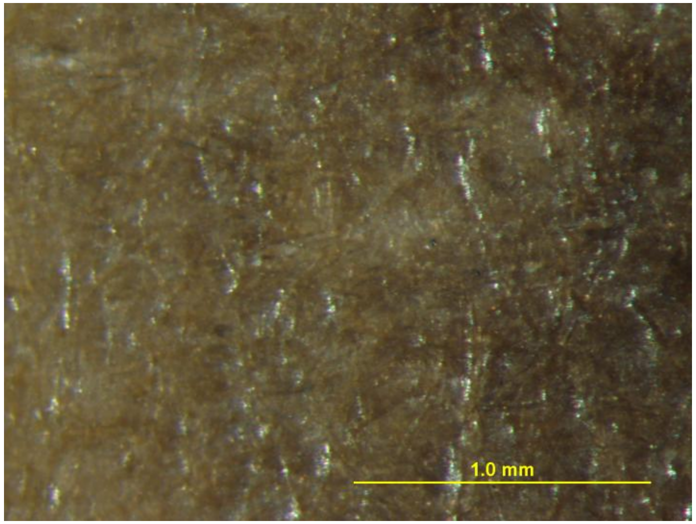
FT-RAMAN STUDY OF PHOTOGRAPHIC COATINGS



ALFRED STIEGLITZ (1864-1946)

COATINGS

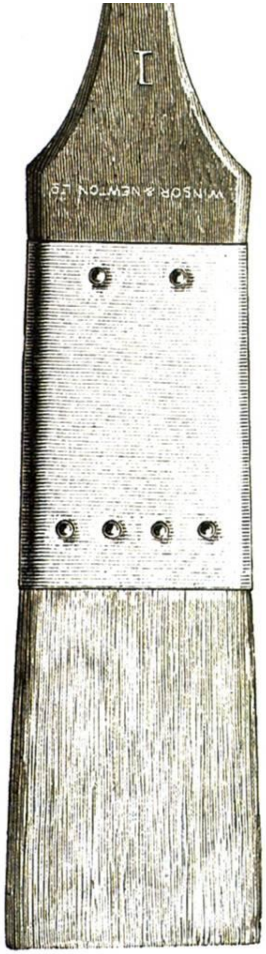


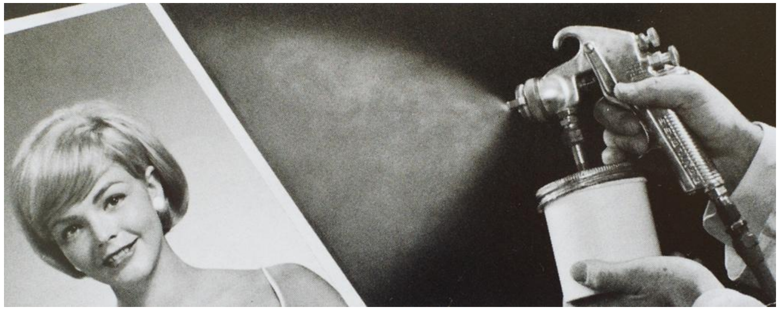


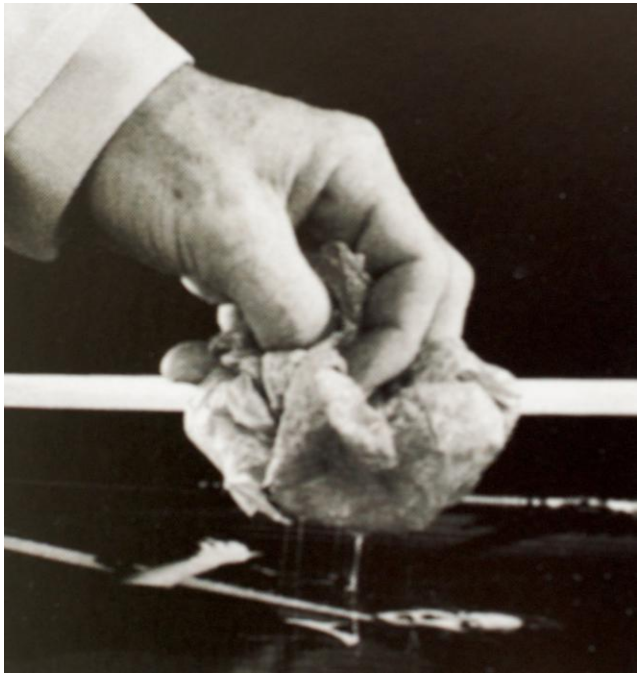
MATERIALS

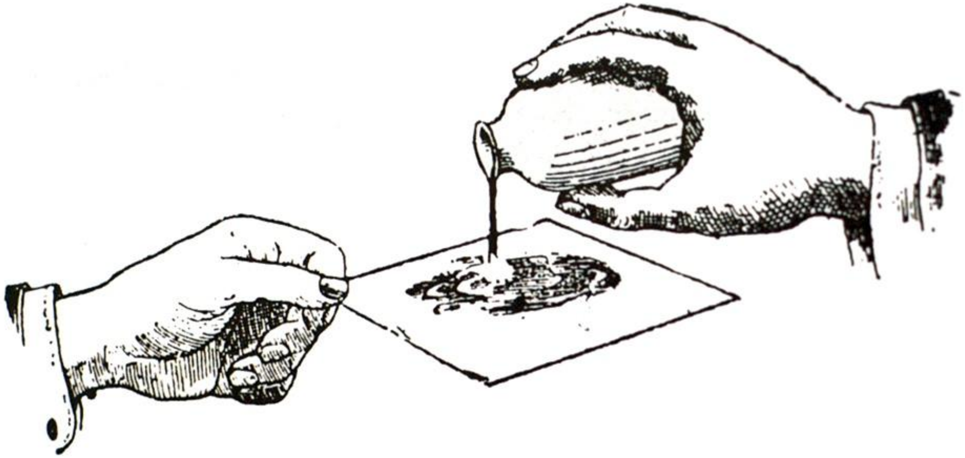
- Waxes *(beeswax, paraffin)*
- Oils *(linseed oil)*
- Resins *(Shellac, Dammar, Rosin, Copal, Canada balsam)*
- Gums *(Arabic gum)*
- Proteins *(gelatin, albumen, less frequently casein)*
- Cellulose derivatives *(Collodion, cellulose nitrate)*
- Synthetic varnishes

COATINGS – APPLICATION METHODS



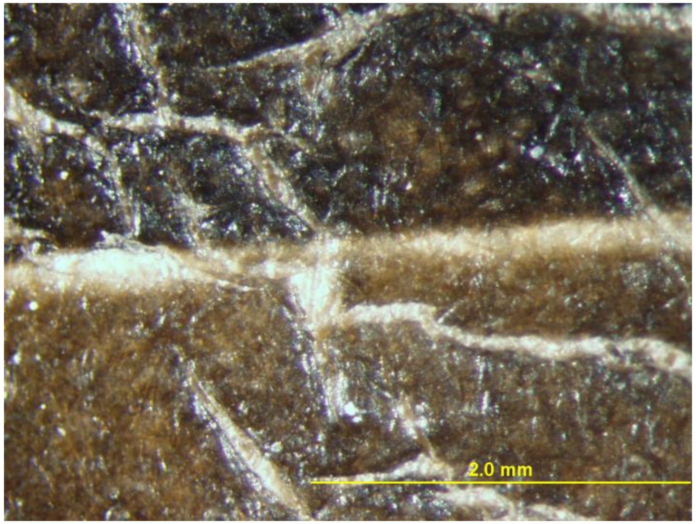


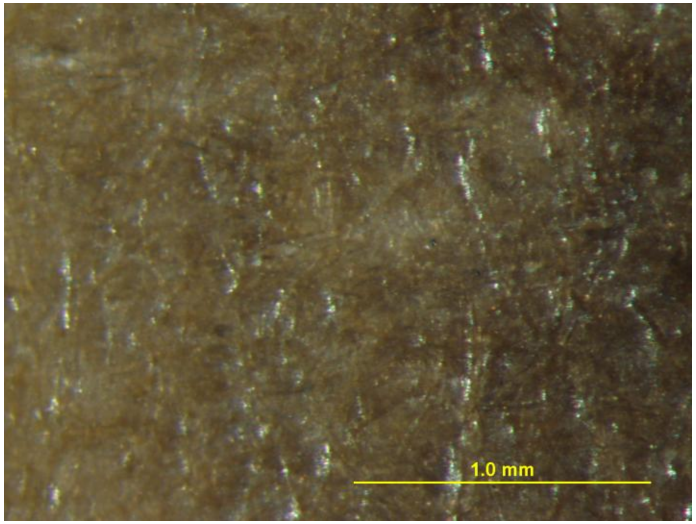




Floating

COATINGS





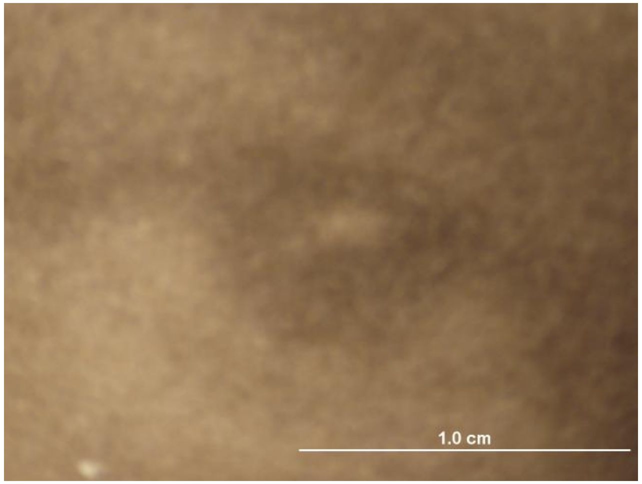
PURPOSES

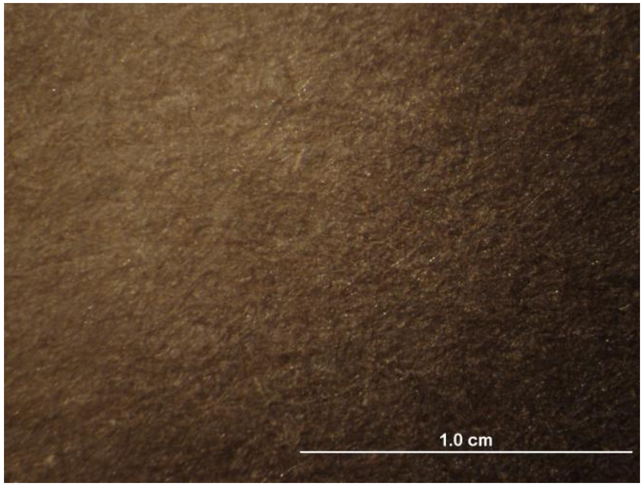
- Aesthetic *increase brilliance and detail, decrease/increase gloss*

- Practical *preparation for hand-coloring*

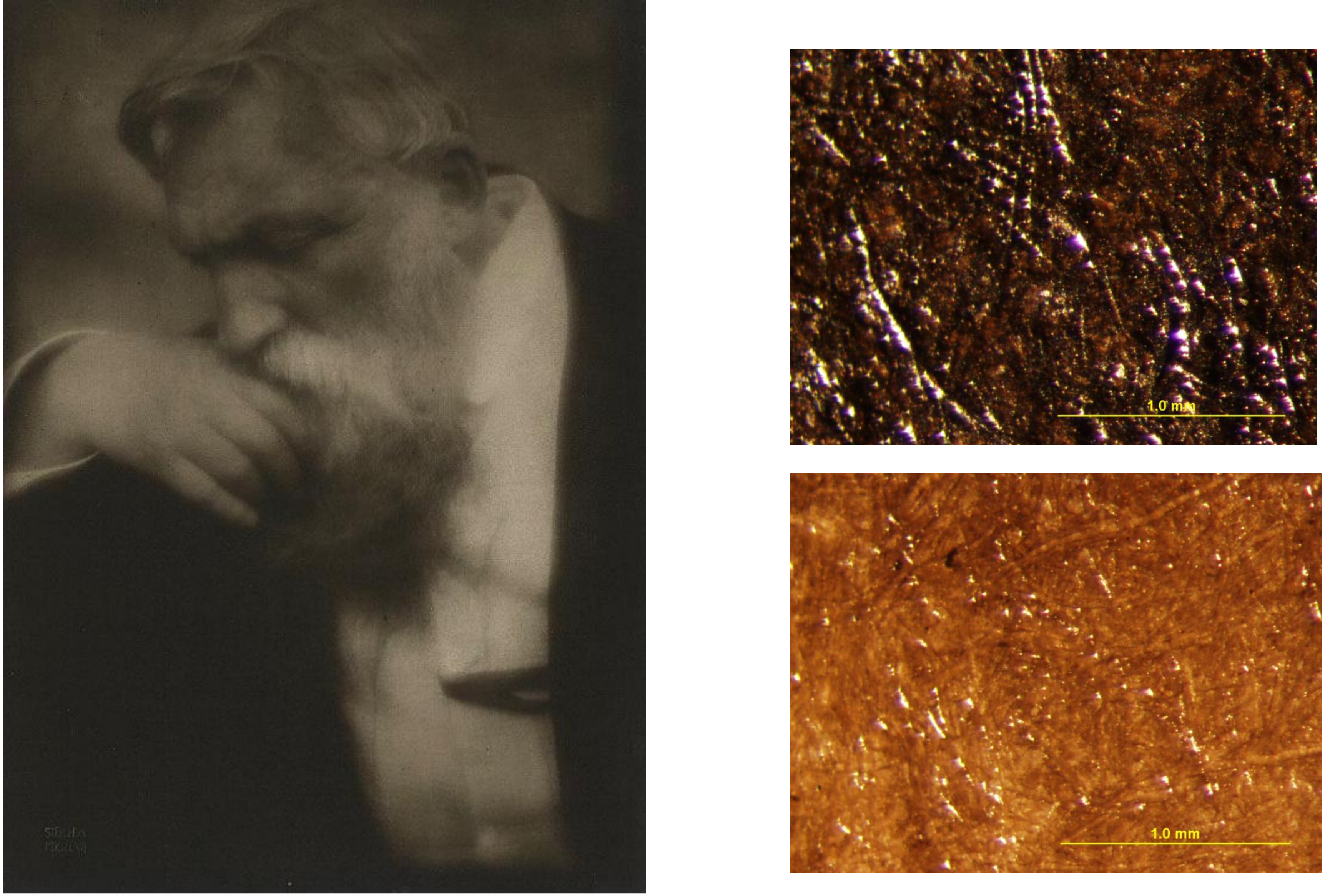
- Protective *from fading, staining, mishandling*

(similarities with picture varnishes)

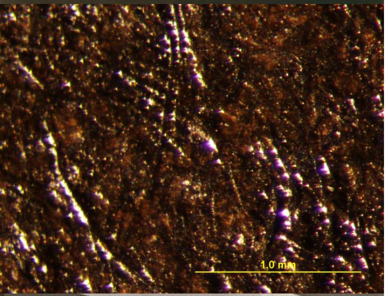


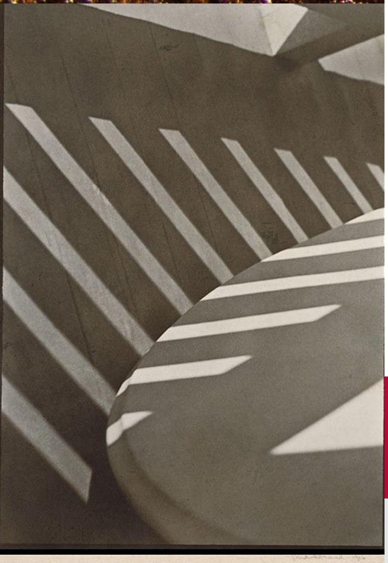


Clarence White, Girl with Muff, 1906 (AIC 1949.856). Pt print



Edward Steichen, Rodin, Paris,1907 (AIC 1949.826) . Pt and Gum dichromate print





OBJECTIVES

Precise identification of coatings to :

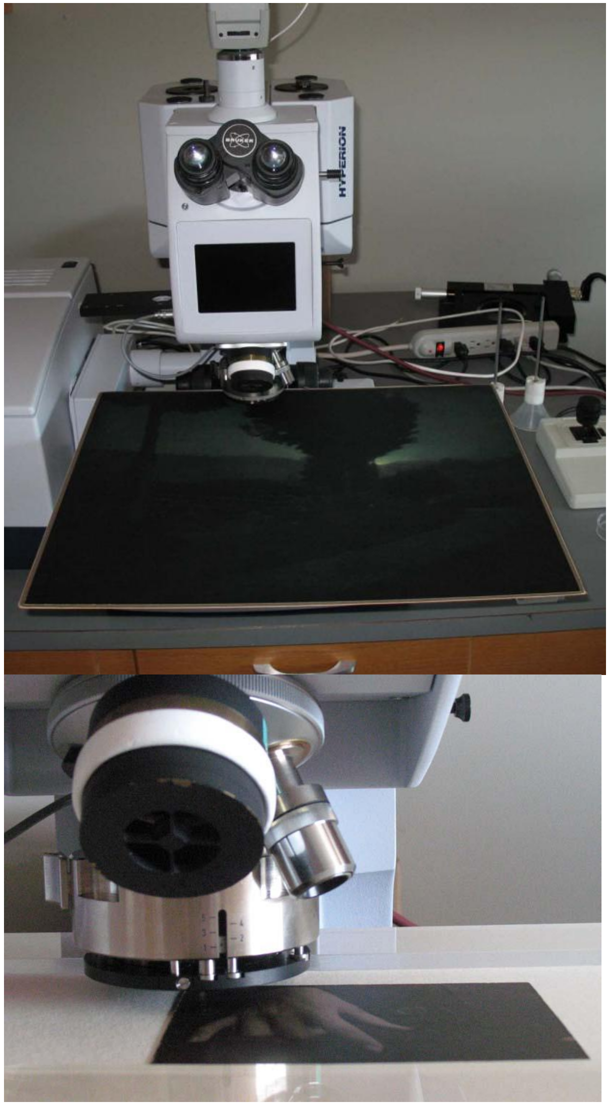
- Elucidate artist’s intention
- Conservation

CONSTRAINTS

- Unlike picture varnishes, sampling is almost never permitted w. photographs
- Coatings are often rather thin

ANALYSIS MUST BE NON INVASIVE

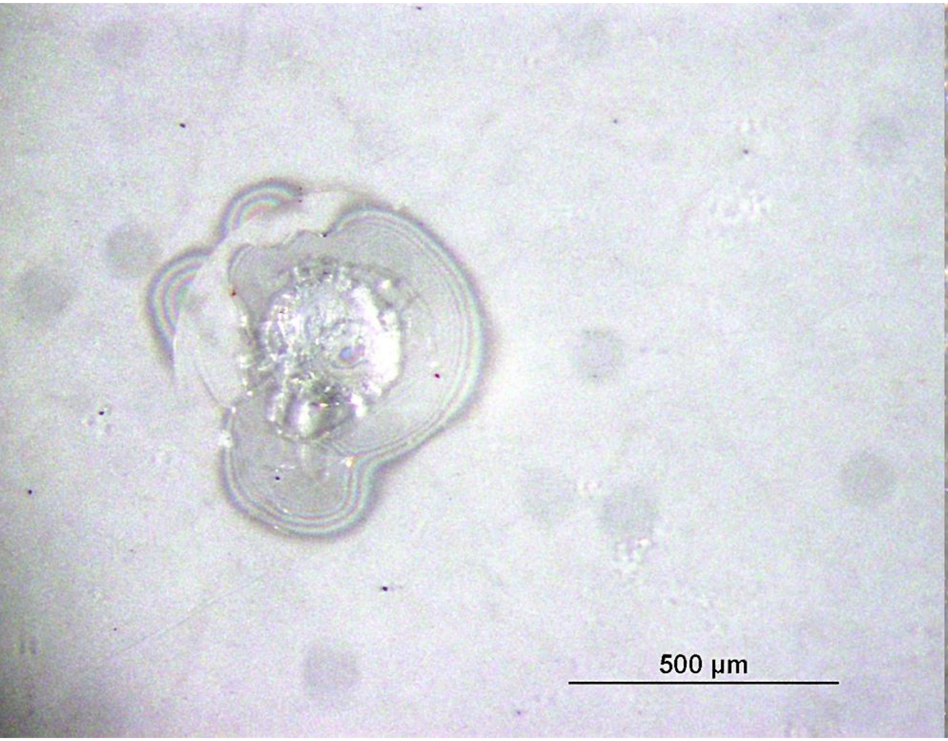
MICRO-ATR

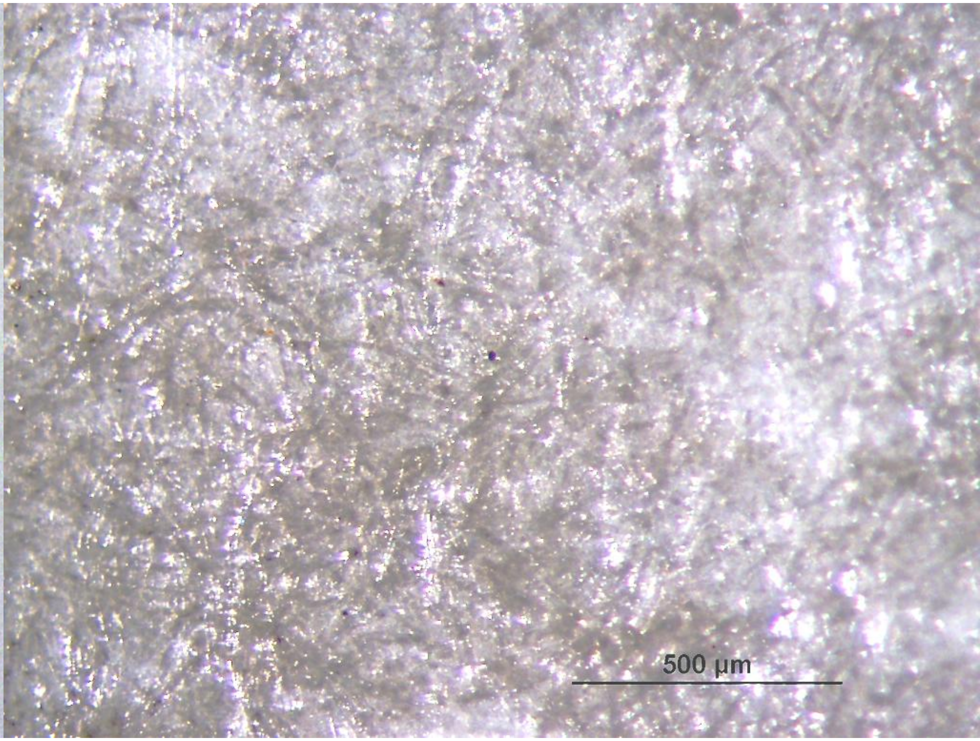


FT-RAMAN SPECTROSCOPY (Dispersive Raman)

Not only non-invasive, but also NON-CONTACT

Micro-ATR





Dammar on POP paper, after ATR

Dammar on Salted paper, after ATR

MATERIALS

- 4 Types of Photo Paper (Chicago Albumen works)

•Salted Paper Print

•Cyanotype

•Albumen

•Gelatin Silver Paper (POP-Printing Out Paper)

- 5 Types of Coating Materials

•Dammar

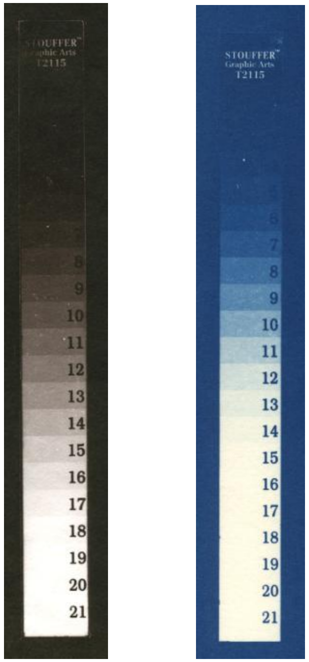
•Gelatin

•Gum arabic

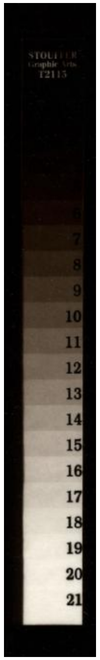
•Linseed oil

•White beeswax

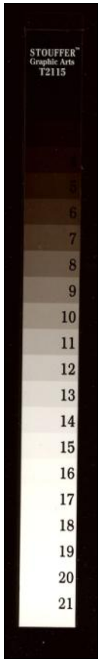
H.G.M. Edwards et al.,Spectrochimica Acta A, 52 (1996) 1639



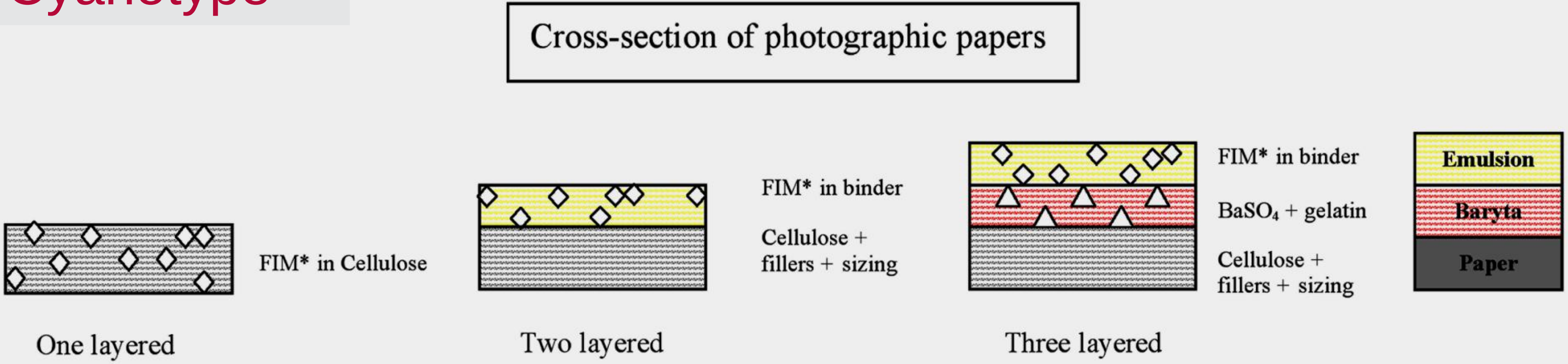
Salted paper
Cyanotype



Albumen

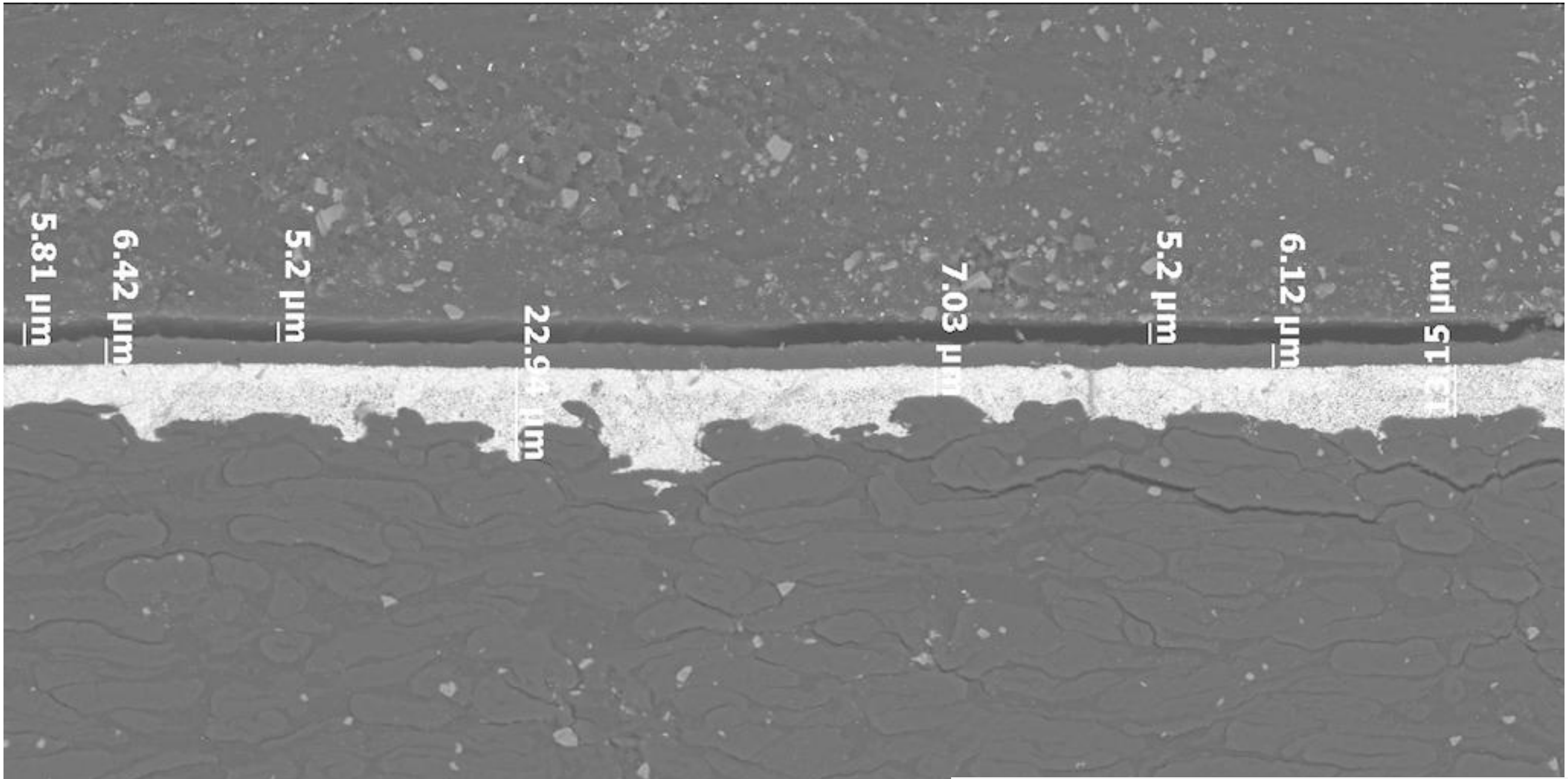


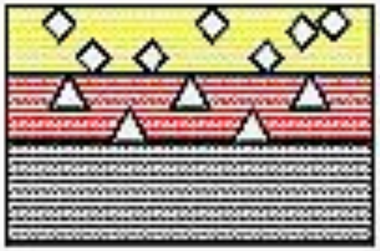
POP



*FIM: final image material

PHOTOGRAPHIC PAPERS



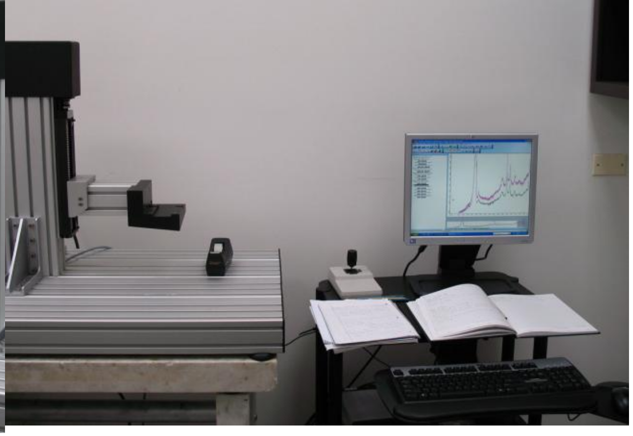


FIM* in binder

BaSO4 + gelatin

Cellulose + fillers + sizing

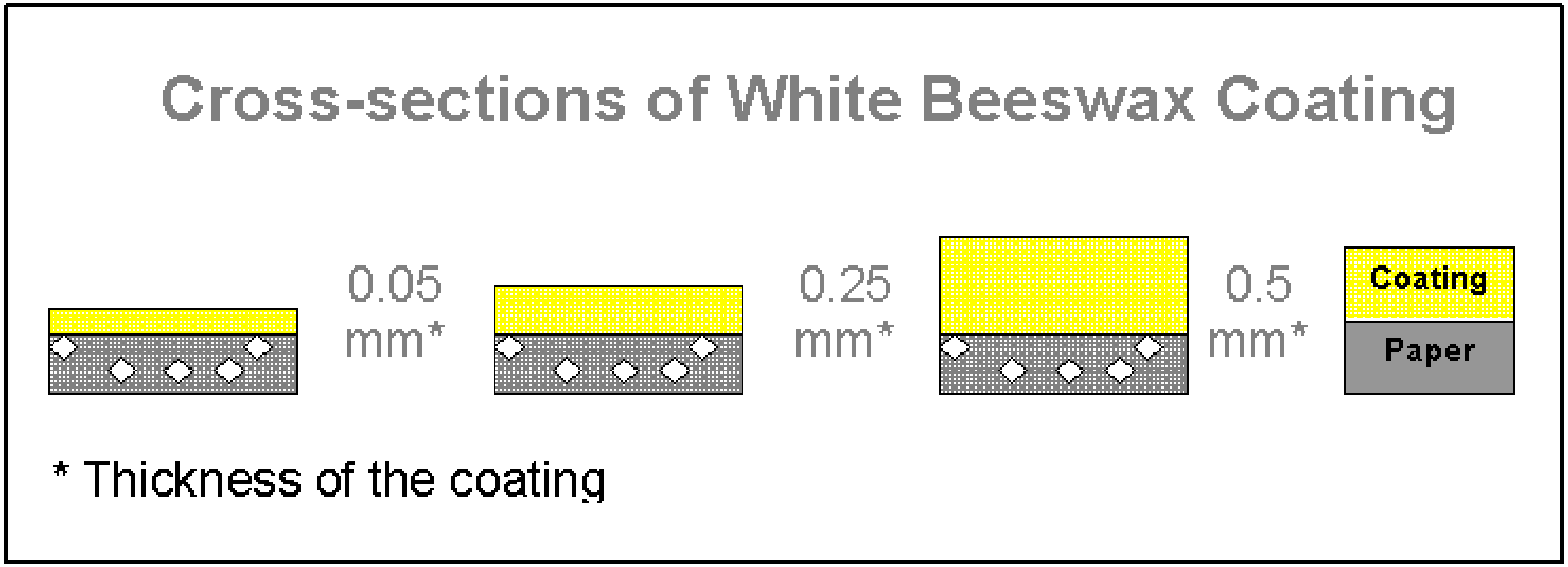
Three layered



FT-RAMAN

- Bruker Vertex 70 FTIR Spectrometer
- Ram II FT-Raman module
- Ramscope III FT-Raman microscope.
- Nd^{3+}/YAG laser (λ_0= 1064 nm)
- High sensitivity, nitrogen cooled Ge detector
- 5000-50000 scans at 4cm^{-1} resolution
- 10x objective,
- nominal laser power of 50-200 mW (actual at sample/2)

SPECTRAL QUALITY/THICKNESS CORRELATION



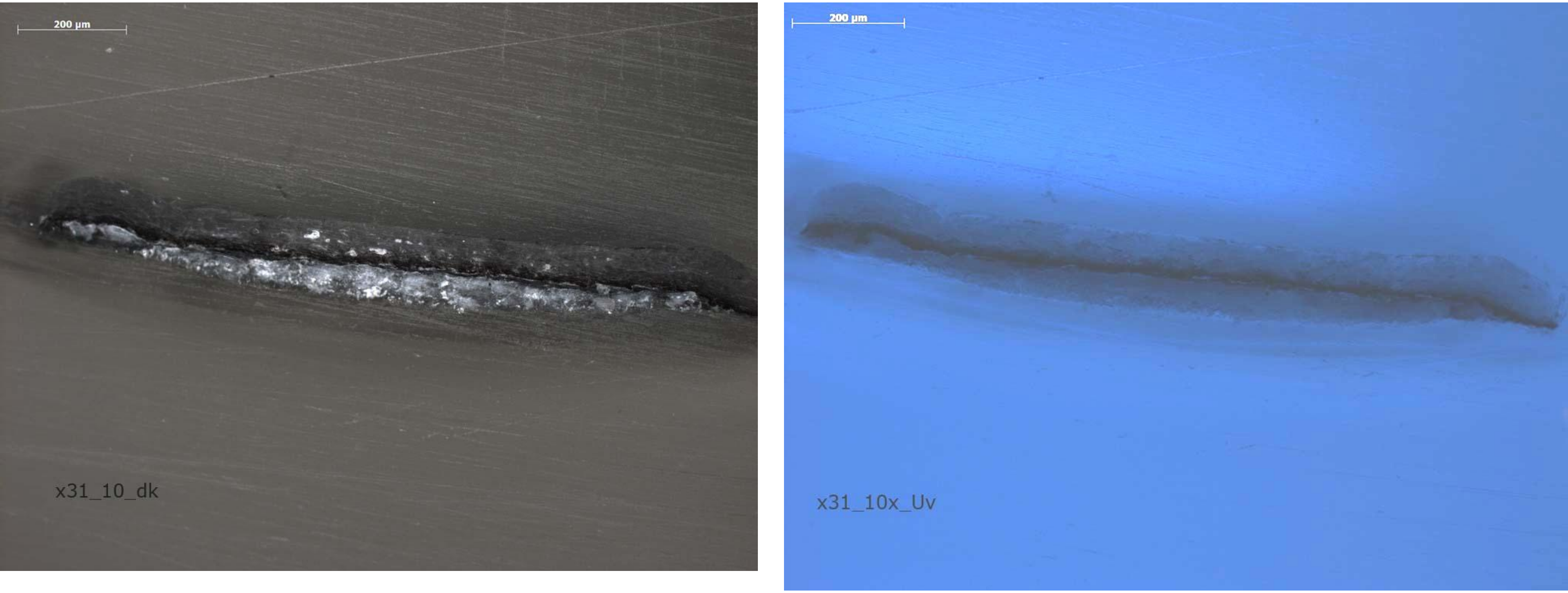
Cross-sections of White Beeswax Coating

* Thickness of the coating

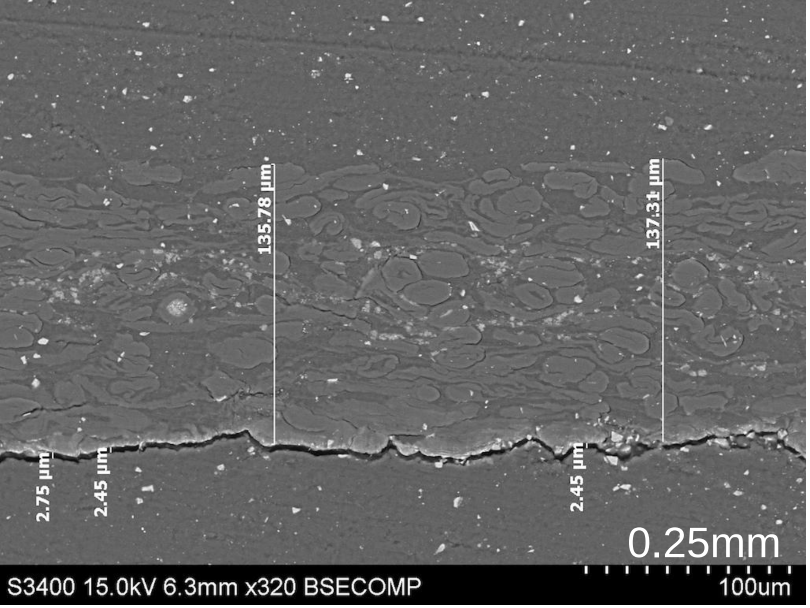
Actual, measured thickness:

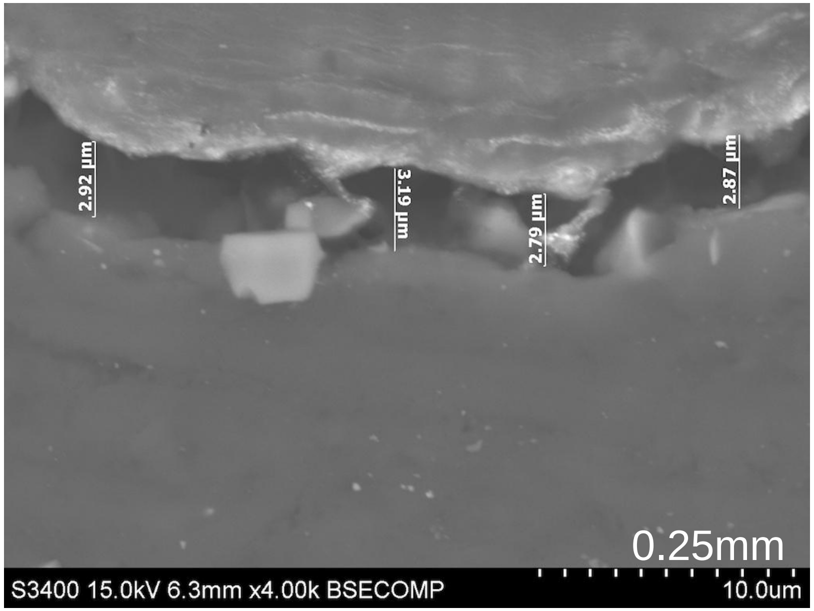
0.05mm= 1.5 µm; 0.25 mm= 2.5 µm; 0.5 mm= 150 µm

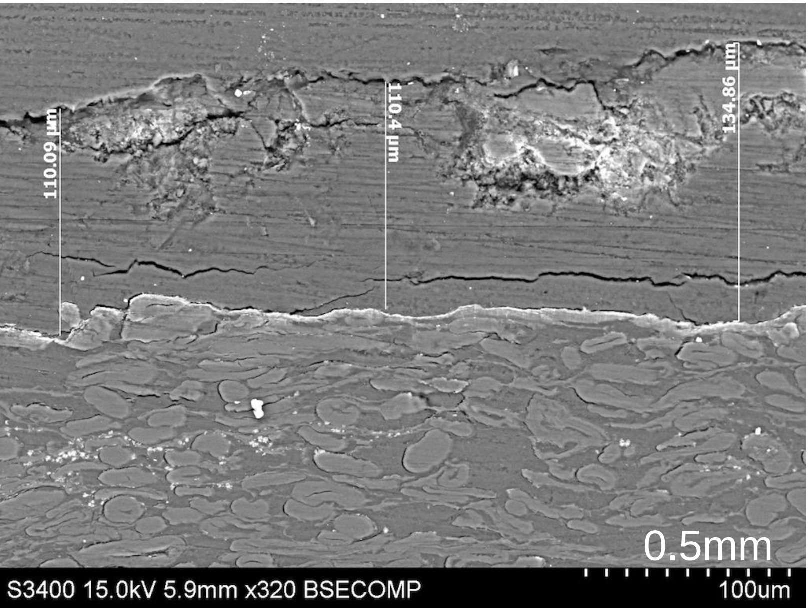
BEESWAX/TURPENTINE
on SALTED PAPER

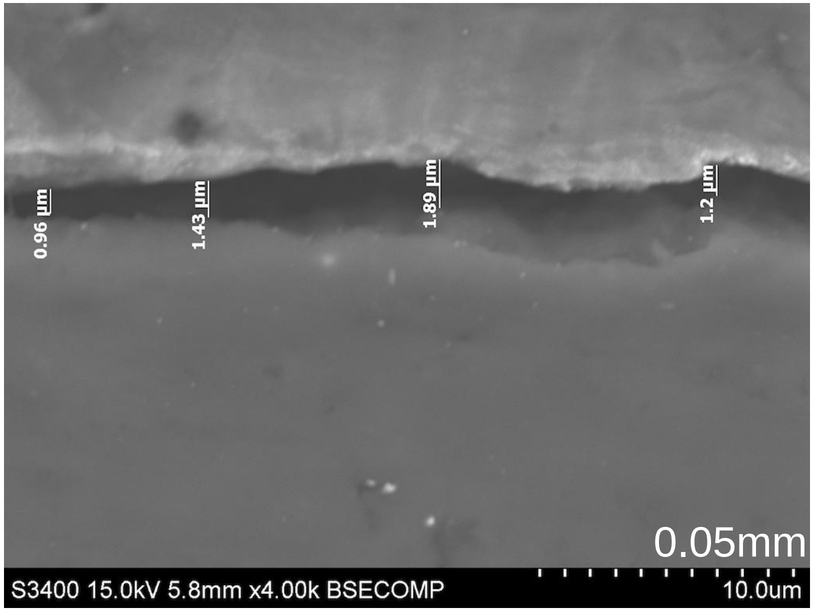


0.5mm beeswax on salted paper









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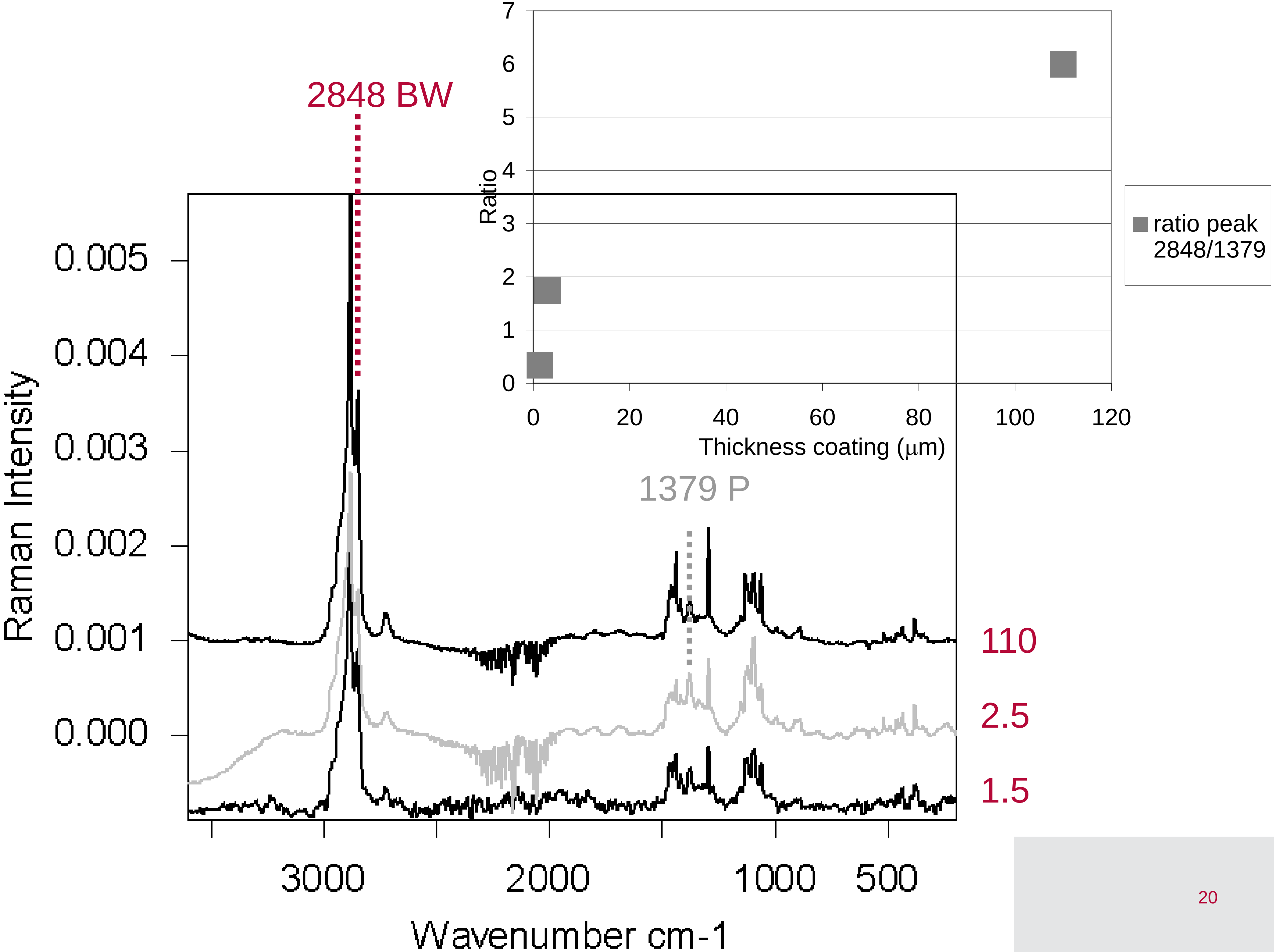
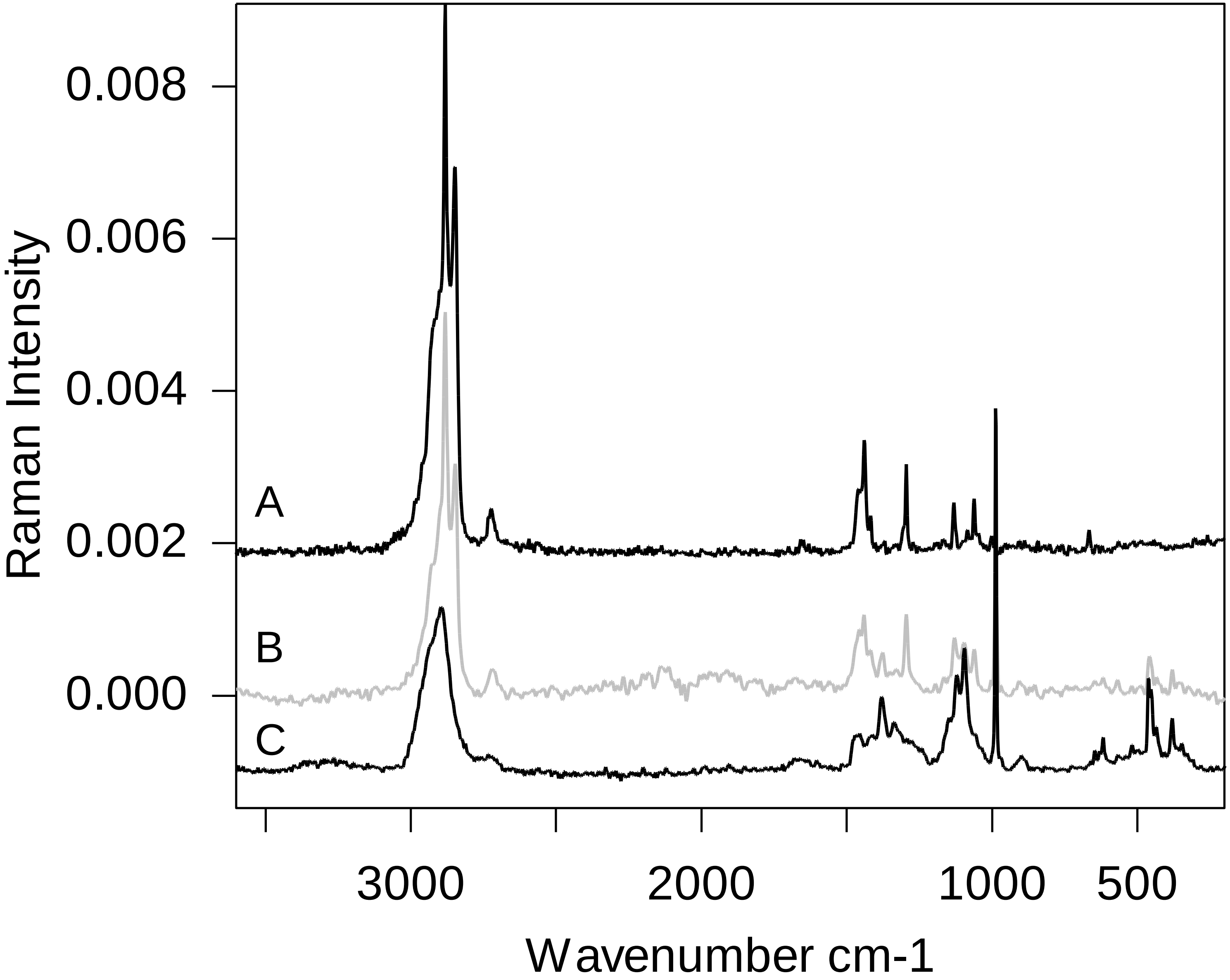
BEESWAX/TURPENTINE on SALTED PAPER

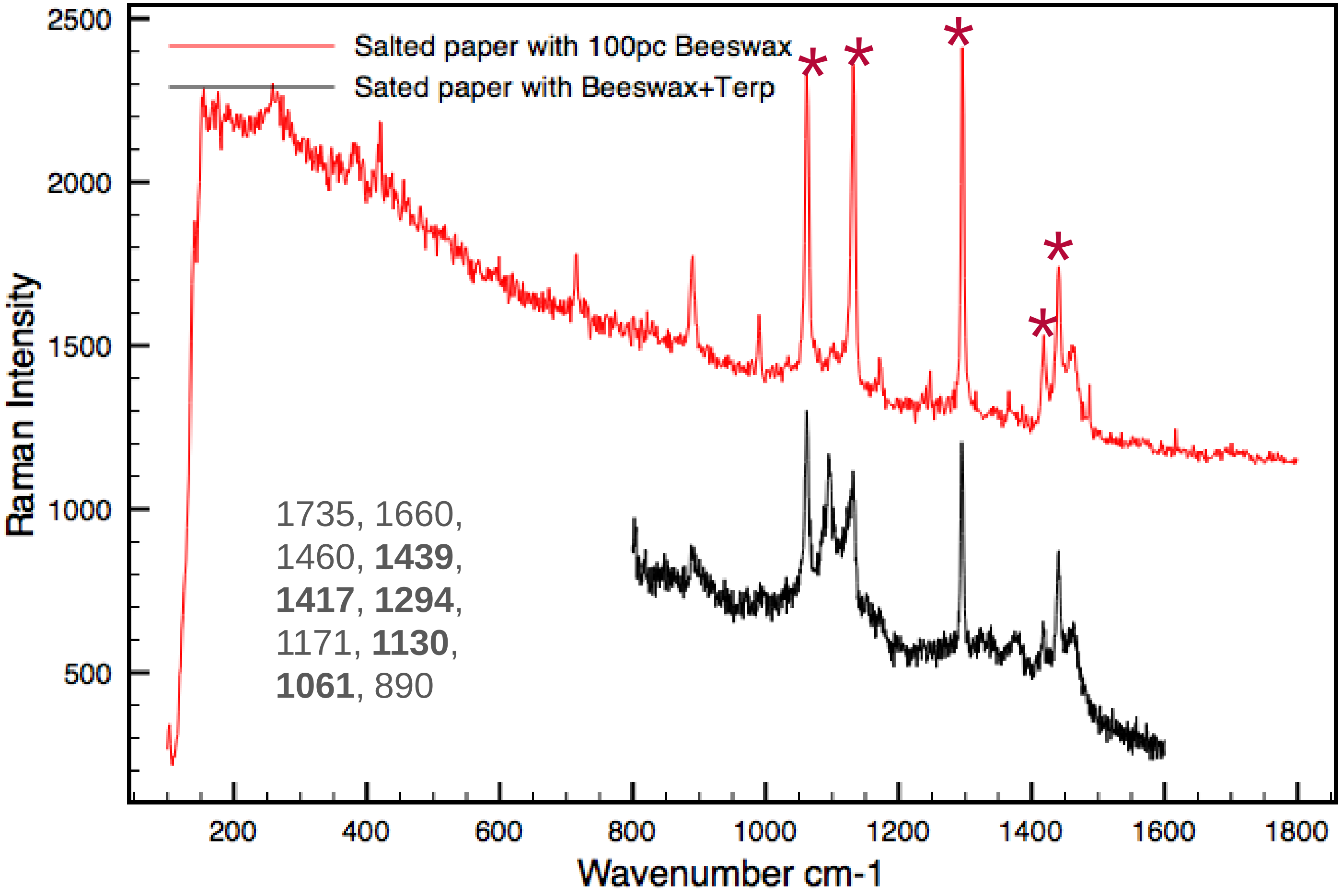

2848 BW
1379 P
Raman Intensity
0.005
0.004
0.003
0.002
0.001
0.000
3000
2000
1000
500
Wavenumber cm-1
110
2.5
1.5
Ratio
7
6
5
4
3
2
1
0
0
20
40
60
80
100
120
Thickness coating (µm)
■ ratio peak 2848/1379



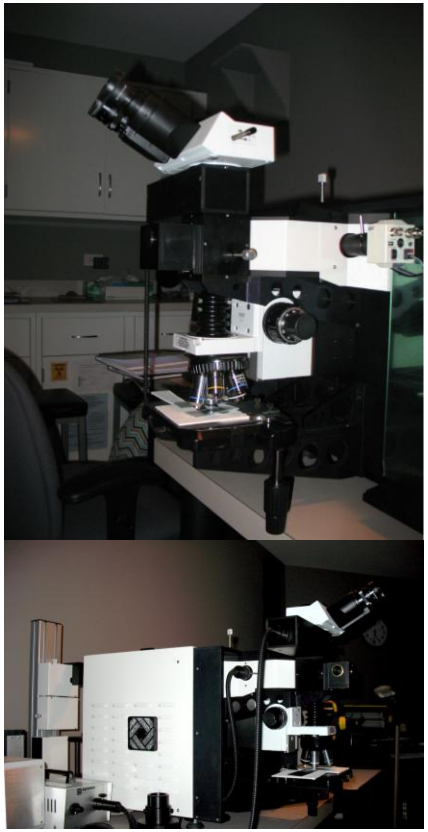
A**:** Reference beeswax; B: Beeswax/Turp. On POP; C: POP paper, no coating

BEESWAX in TURPENTINE

DETECTION CAPABILITIES- DISPERSIVE RAMAN



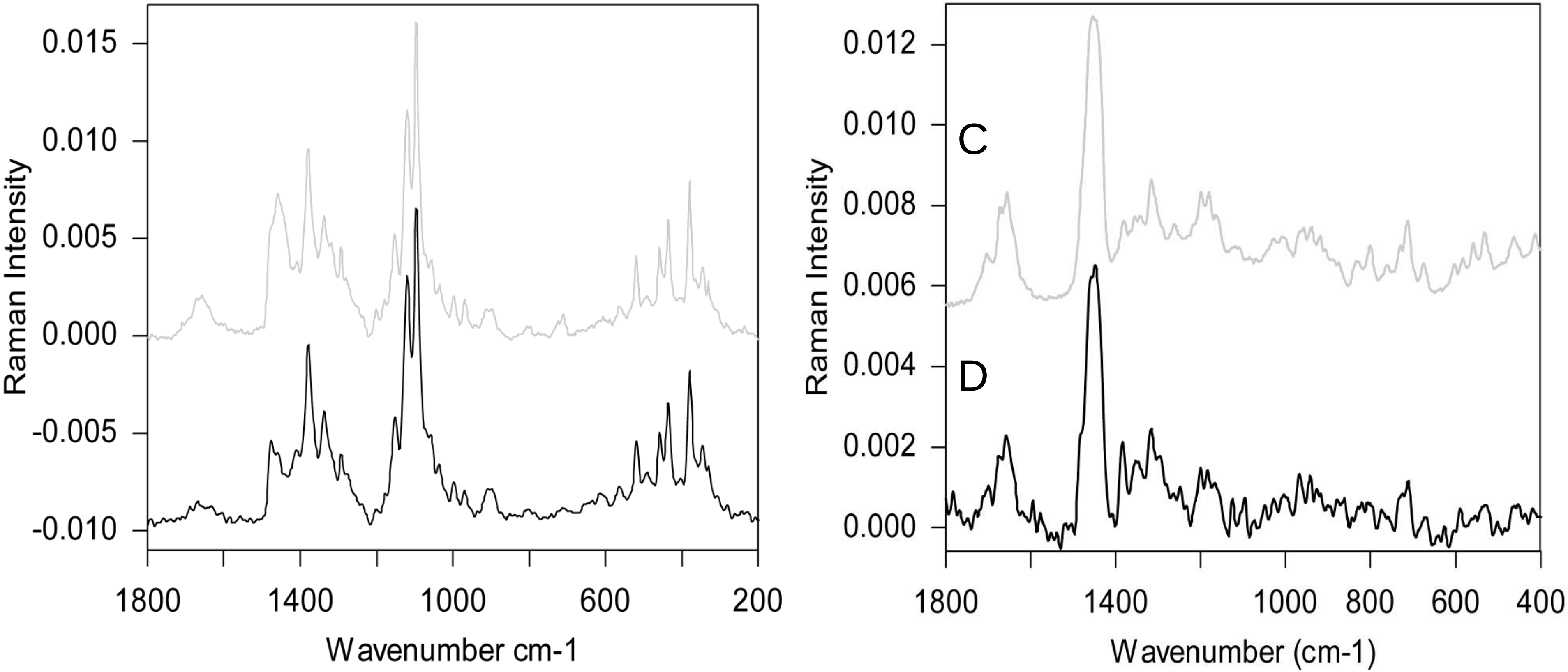
1735, 1660, 1460, **1439**, **1417**, **1294**, 1171, **1130**, **1061**, 890



Vandenabeele, P. et al., 2000. *Analytica Chimica Acta*, 407(1-2), pp.261–274

BEESWAX in TURPENTINE

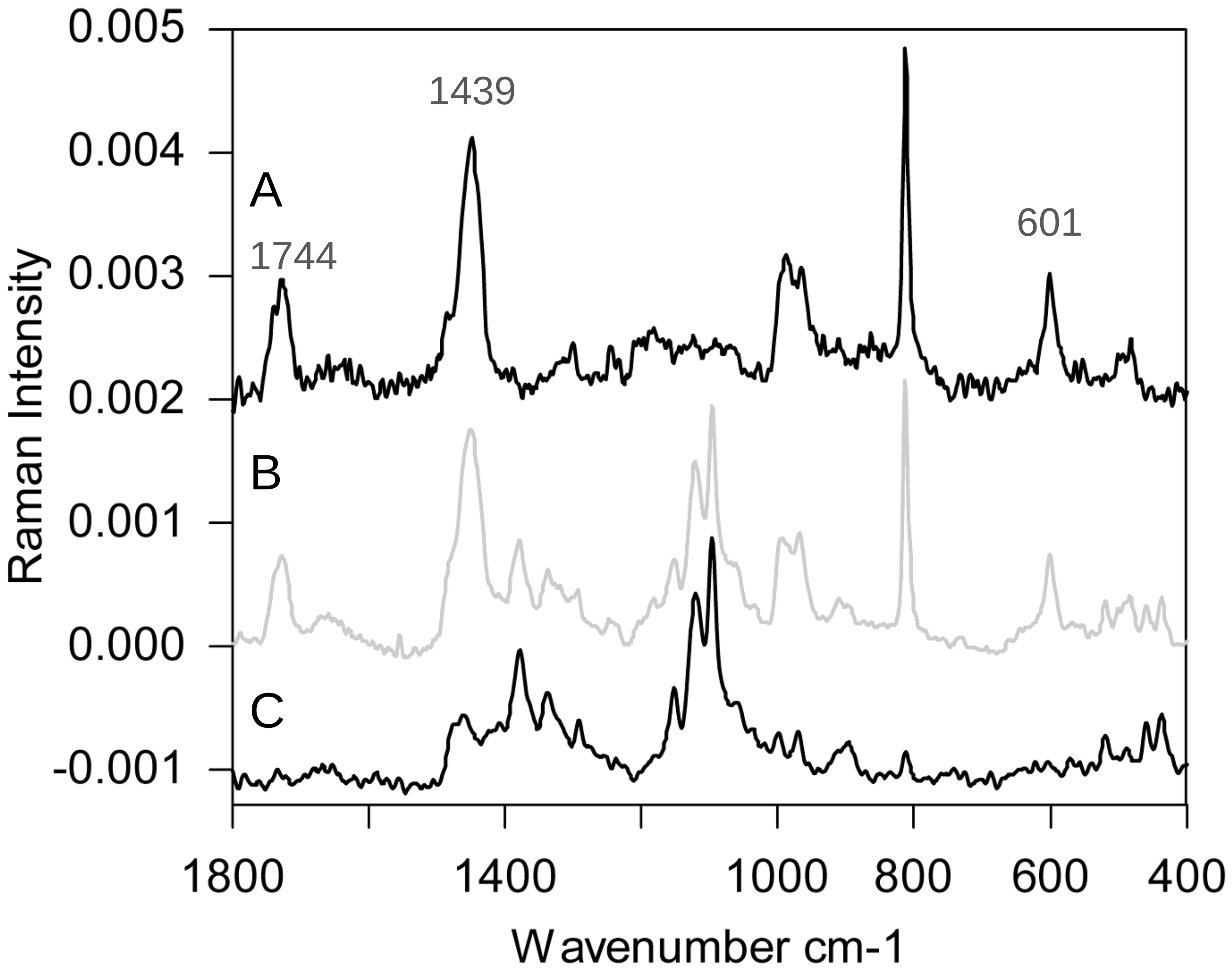
SPECTRAL SUBTRACTION: CYANOTYPE



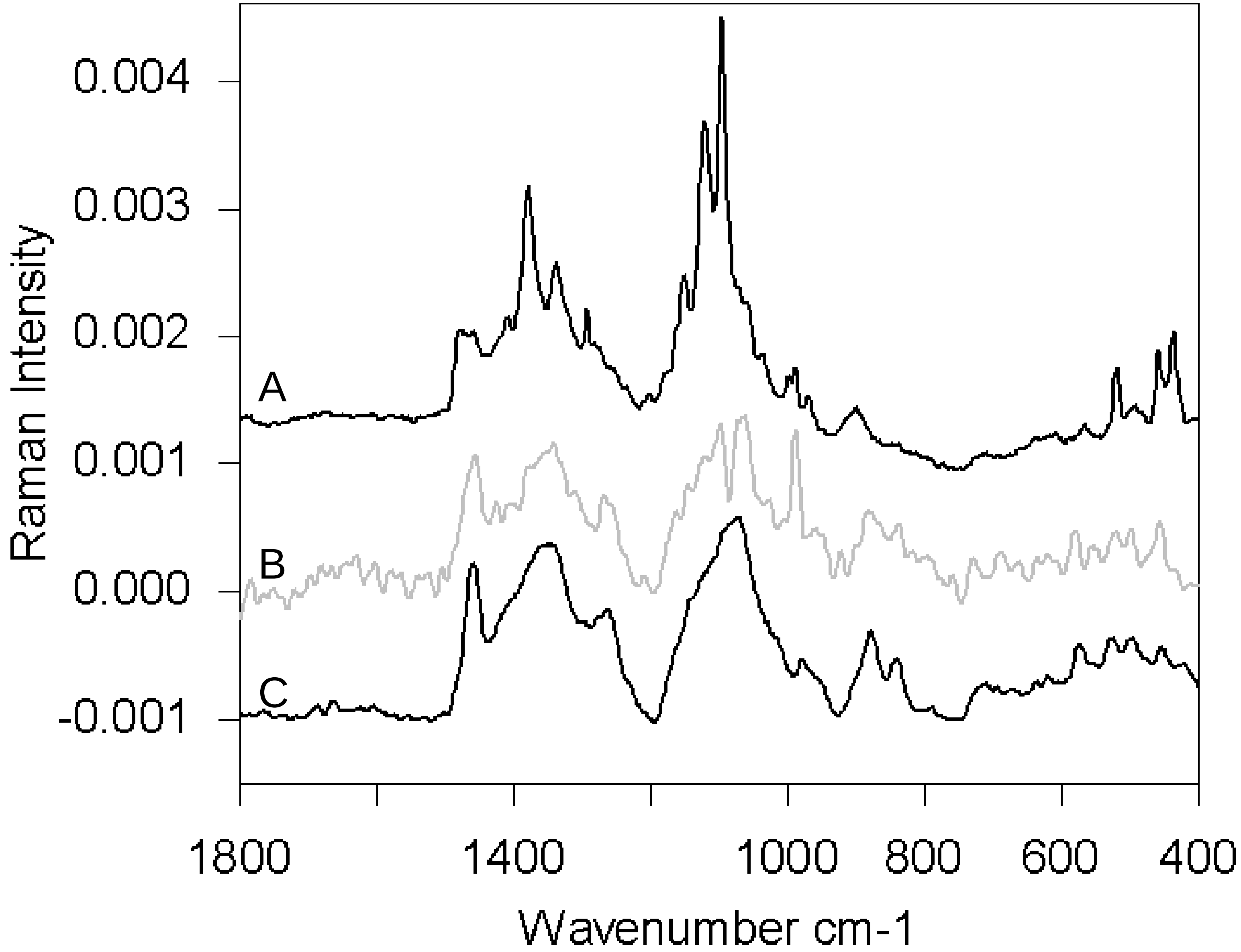
A: Dammar on cyanotype; B: Uncoated cyanotype paper

C: Dammar reference; D: Dammar on cyanotype minus paper

DETECTION CAPABILITIES- FT-RAMAN

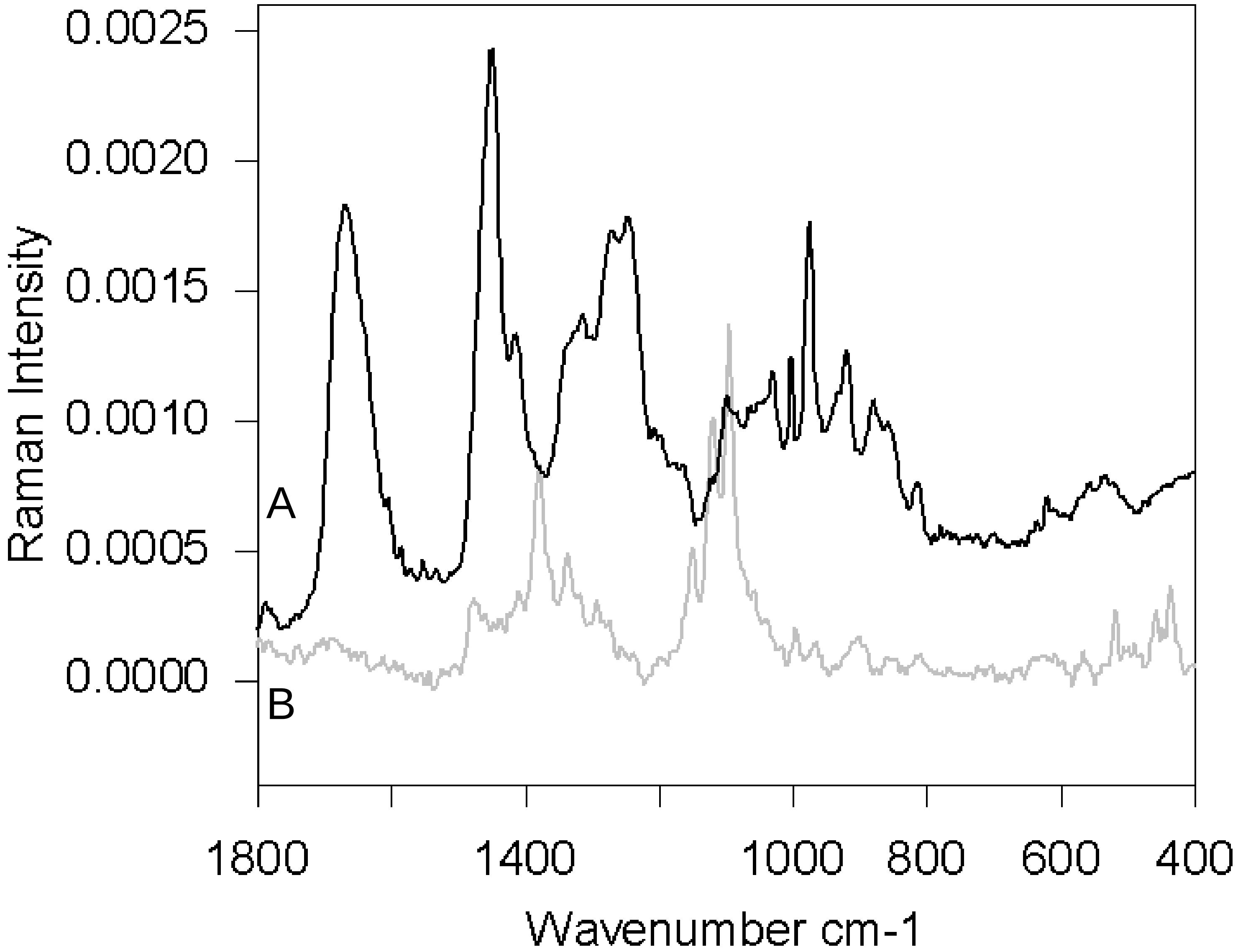


A**:** Spectral subtraction; B: Linseed oil on Albumen paper; C: Albumen paper, no coating



A**:** Gum Arabic on salted paper; B: Spectral subtraction; C: Gum Arabic reference

GUM ARABIC



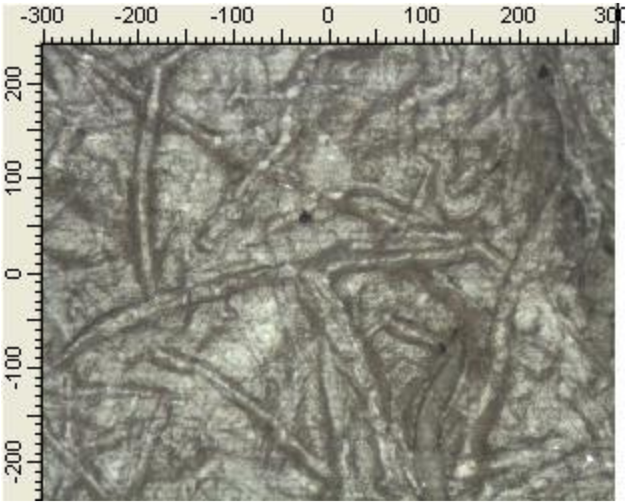
A**:** Gelatin reference; B: Gelatin on Salted paper

DETECTION CAPABILITIES

	One Layered	**Two layered**	**Three layered**
Dammar	FT-Raman ATR-FTIR Disp. Raman	FT-Raman ATR-FTIR	ATR-FTIR
Gelatin	ATR-FTIR	N/A	N/A
Gum Arabic	FT-Raman ATR-FTIR	ATR-FTIR	ATR-FTIR
Linseed Oil	FT-Raman ATR-FTIR Disp. Raman	FT-Raman ATR-FTIR	FT-Raman ATR-FTIR
White Beeswax + turpentine	FT-Raman ATR-FTIR Disp. Raman	FT-Raman ATR-FTIR	FT-Raman ATR-FTIR

CASE STUDIES

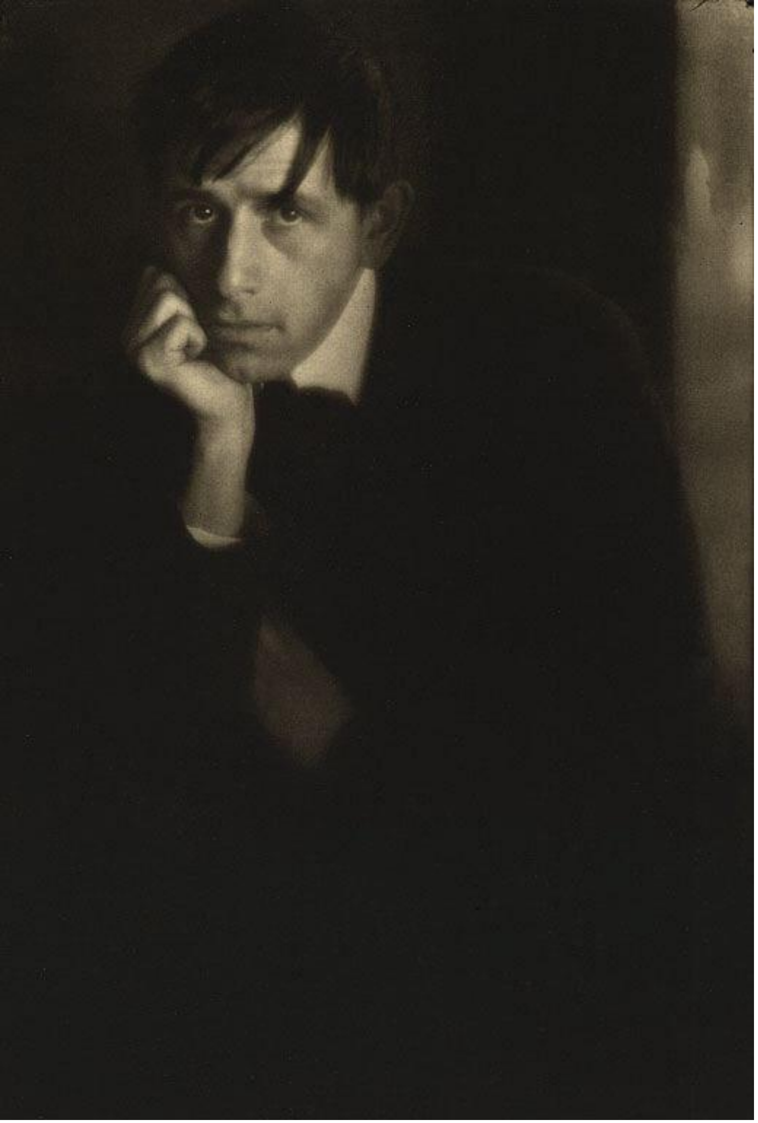
A. Stieglitz, Portrait, 1922 (AIC 1947.716) Pd print



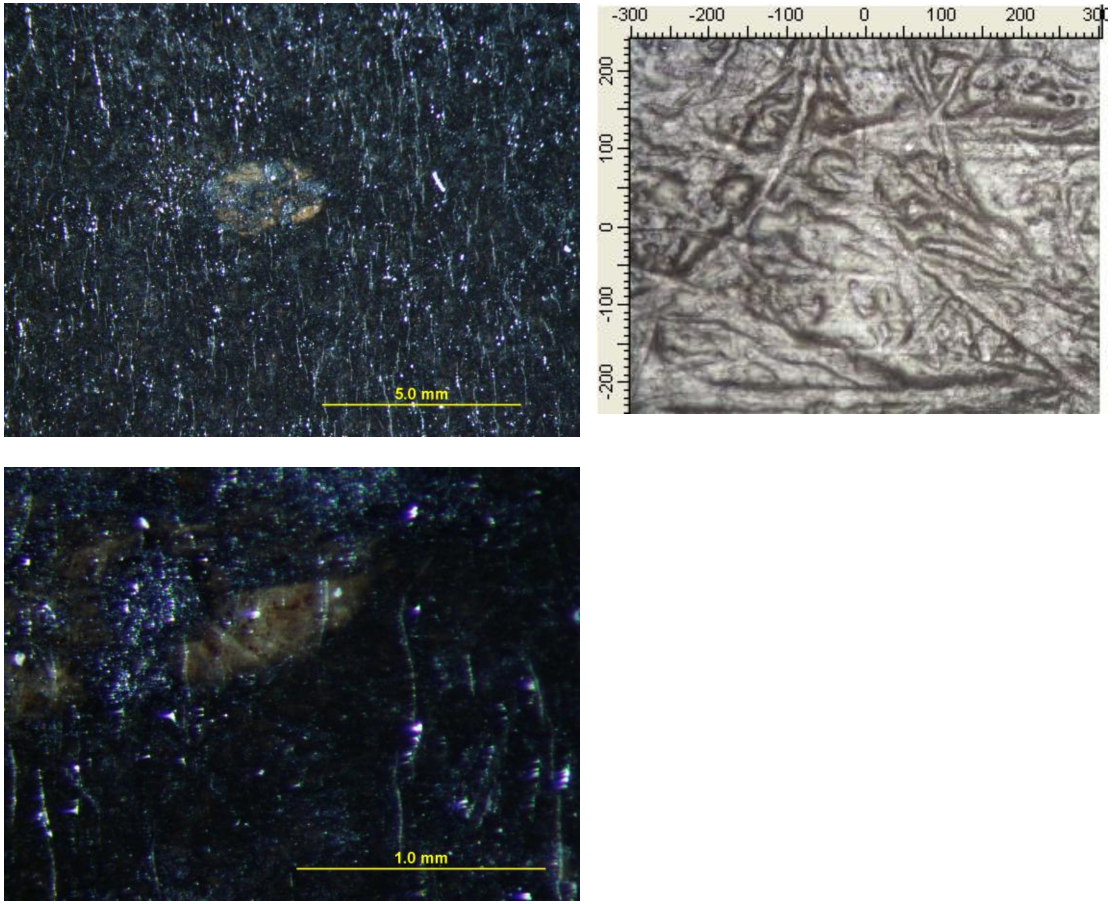
Protein sizing

Extremely thin layer of wax (diamond cell FTIR)

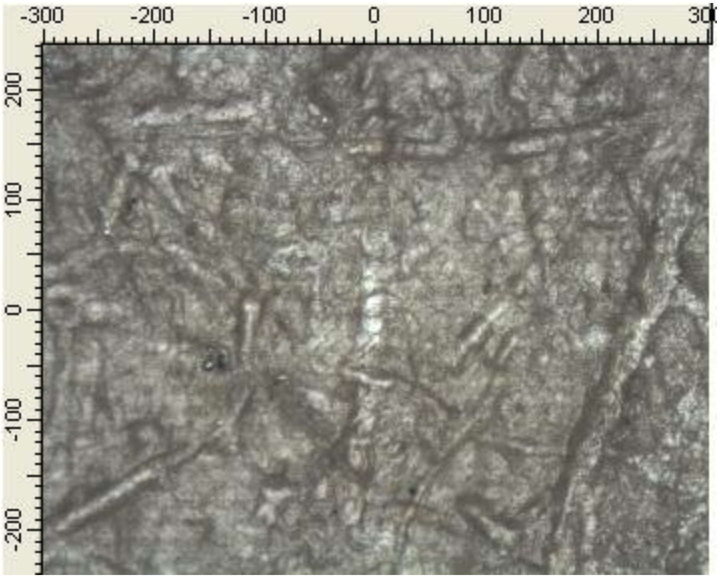
Micro-ATR: Gum Arabic



E. Steichen, Portrait of Clarence White, 1908 (1949.828) Pt print

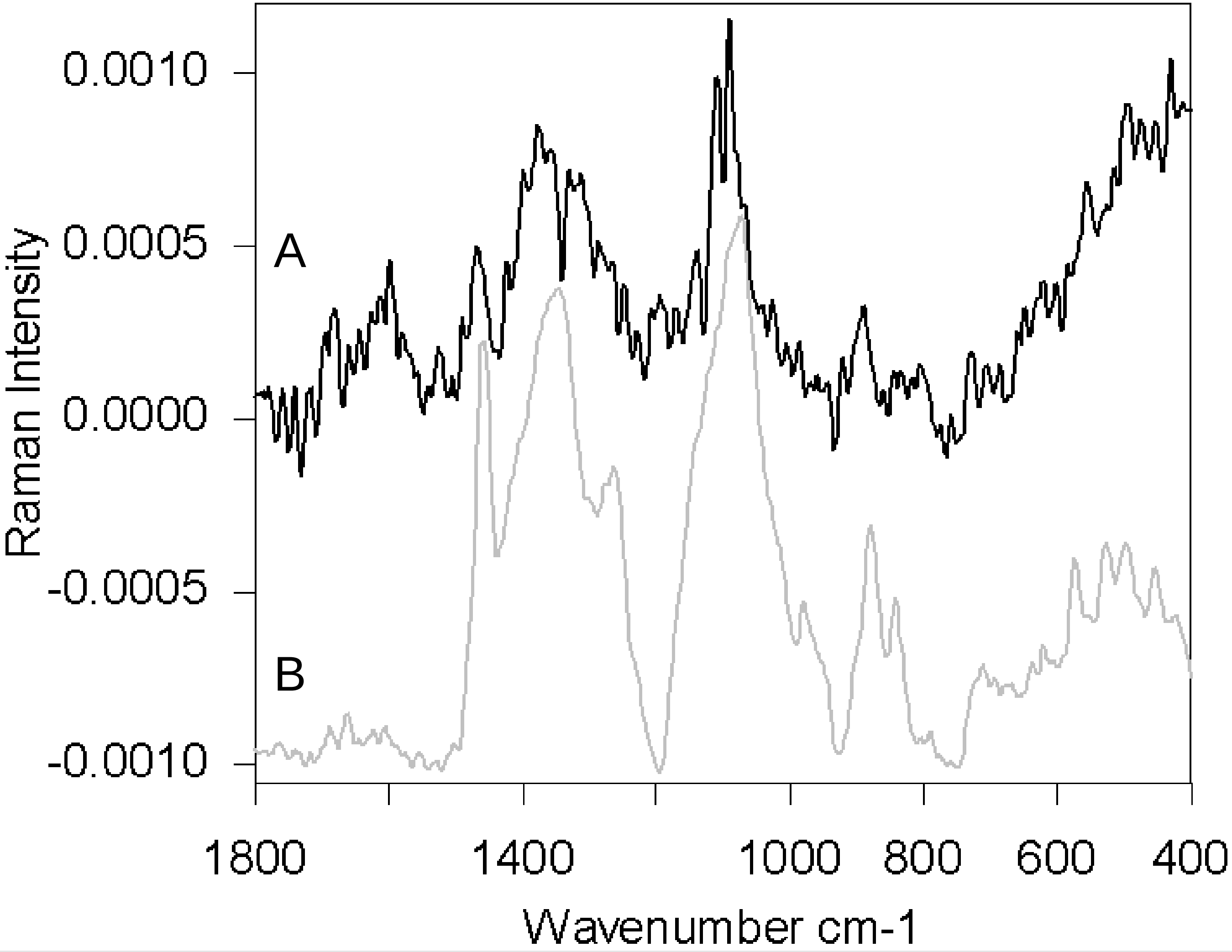


A. Stieglitz, Georgia O'Keeffe, 1918 (1949.743) Pd print



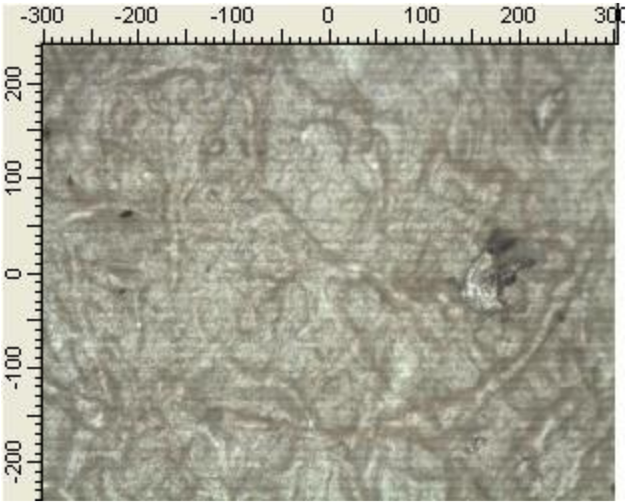
ATR-very thin layer of beeswax and gum arabic?

FT-Raman: Gum Arabic



A**:** 1949.743 Spectral subtraction;

B: Gum Arabic reference

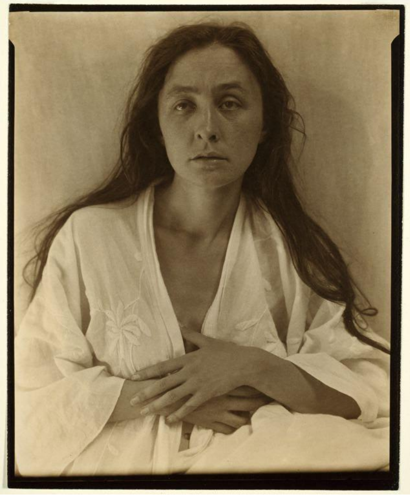


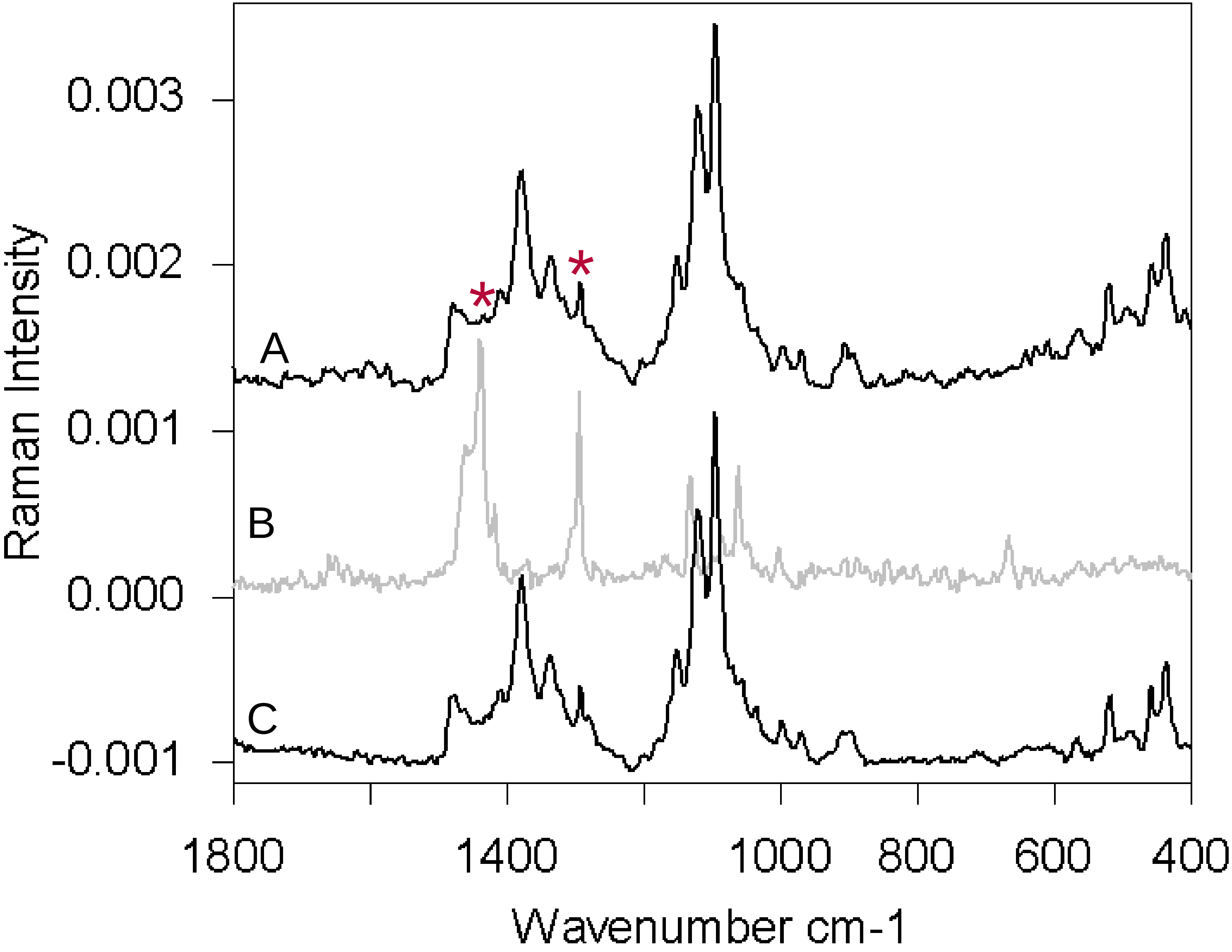
Micro-ATR:

layer of wax

A. Stieglitz, Georgia O'Keeffe 1918 (1949.745A) Pd print

FT-Raman: Beeswax



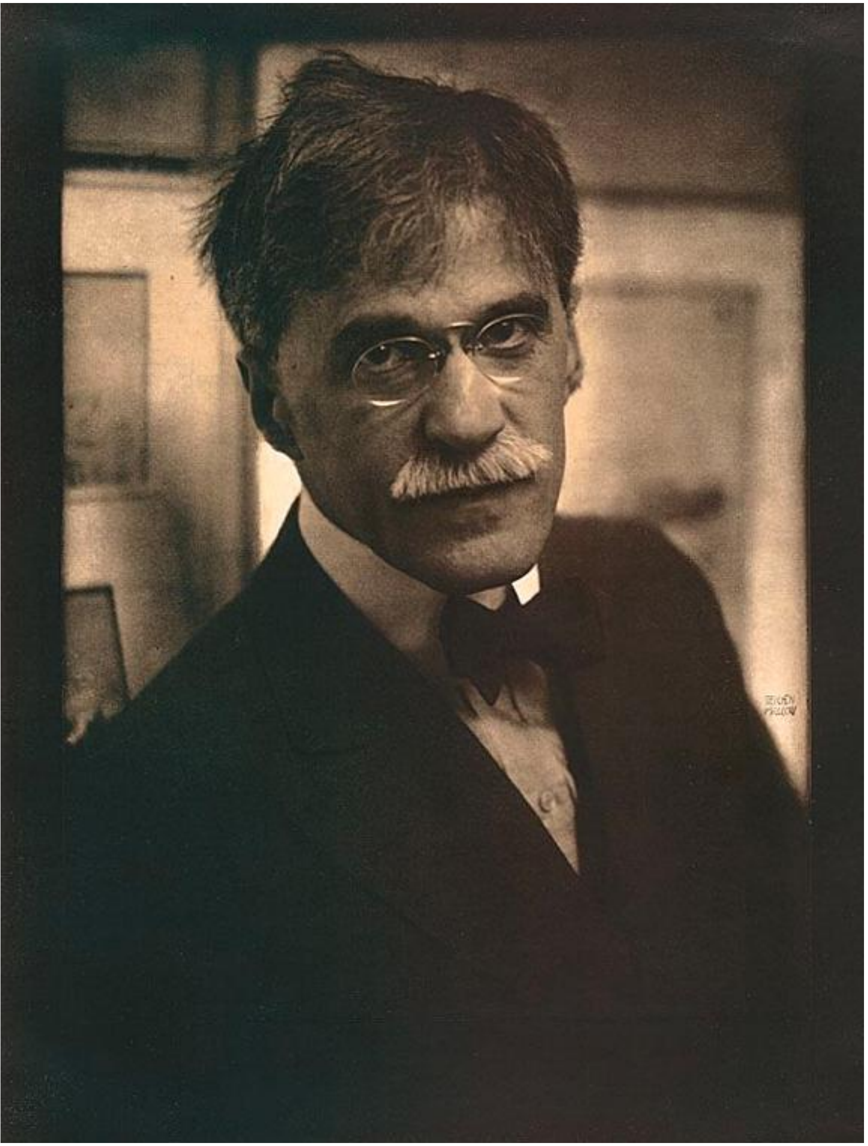


A**:** 1949.745A;

B: Beeswax reference;

C: salted paper reference

CONCLUSIONS

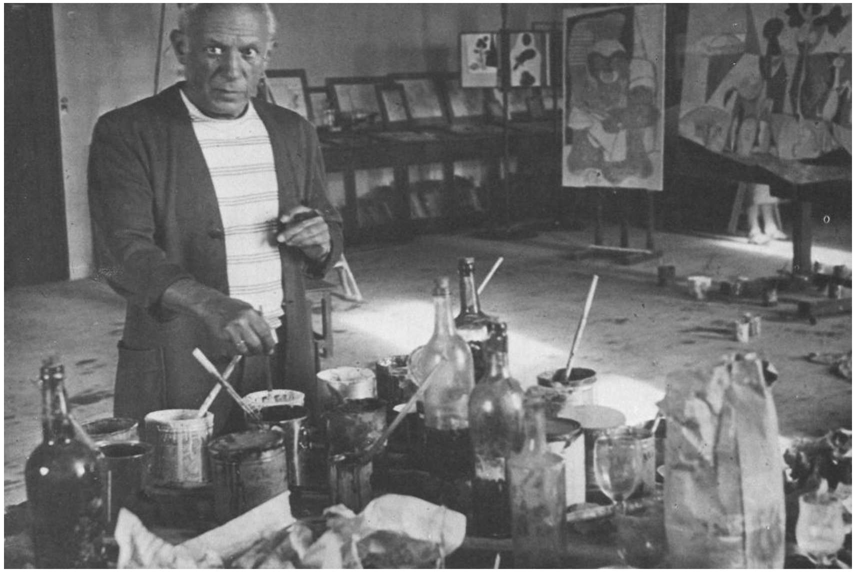


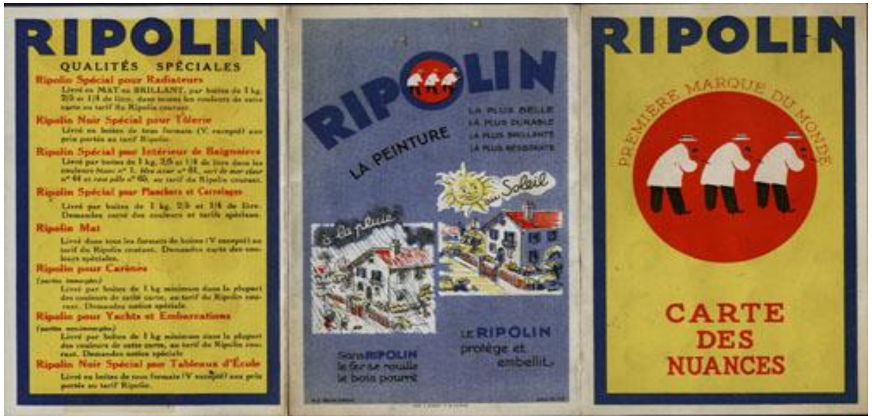
- Micro-ATR- universal technique, but can cause micro-damage
- FT-Raman detects drying oils, waxes, resinous media and gums on Photograph papers (Albumen, Salted paper, POP paper and Cyanotype) only when thickness is >3 μm
- Long collection times, interference from paper substrate make data collection and interpretation laborious
- Best results on salted papers (including dispersive Raman)

FT-RAMAN/ FTIR RIPOLIN

Red Armchair, 1931

Figure, 1935





RIPOLIN

QUALITÉS SPÉCIALES

Ripolin Spécial pour Radiateurs

Ripolin Noir Spécial pour Tôlerie

Ripolin Spécial pour Intérieur de Baignoires

Ripolin Spécial pour Planchers et Carrelages

Ripolin Mat

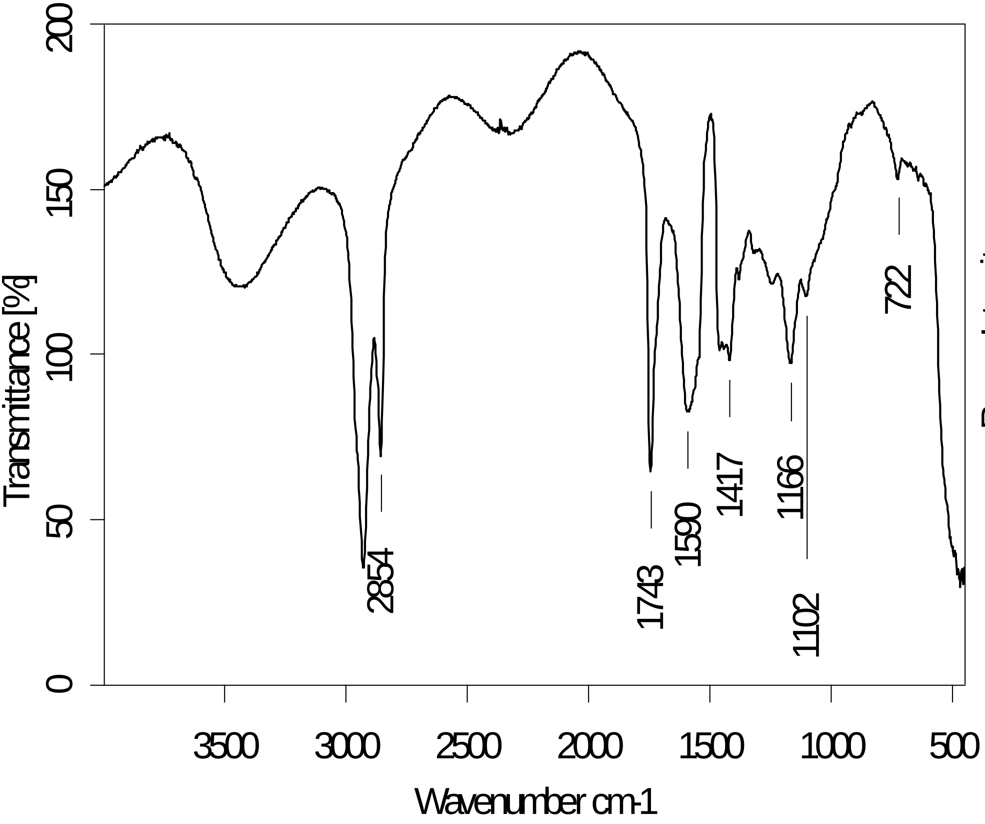
Ripolin pour Carènes

Ripolin pour Yachts et Embarcations

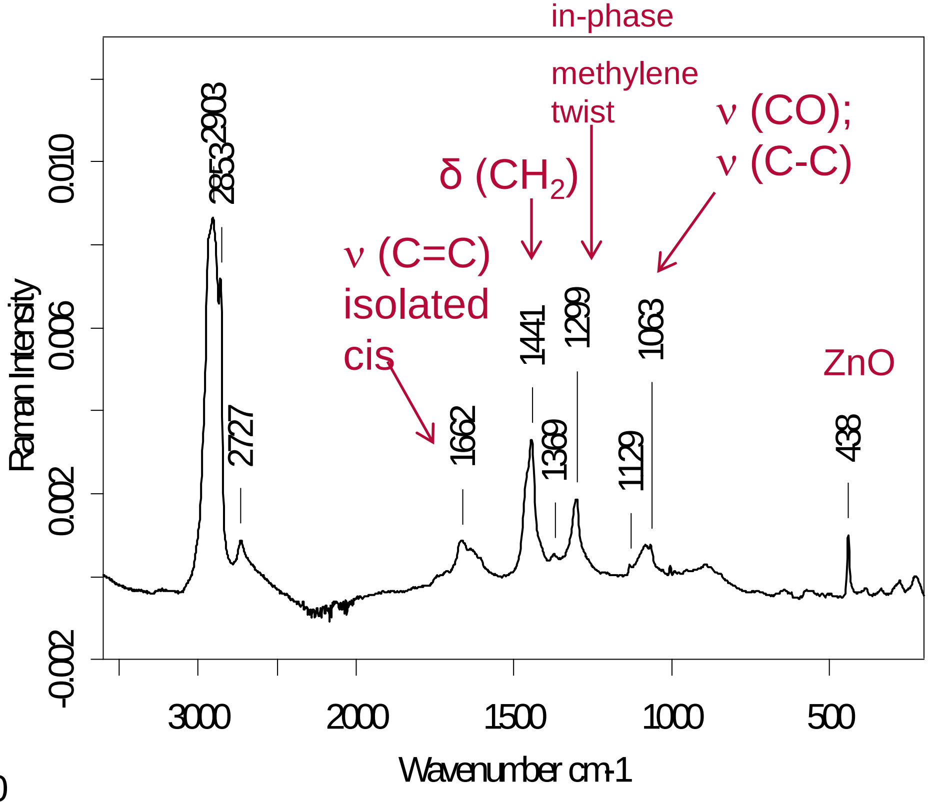
Ripolin Noir Spécial pour Tableaux d'École

LES NUANCES 27, 78, 13, 54 NE SONT PAS RECOMMANDEES POUR L'EXTERIEUR

RIPOLIN blanc de neige - brochure



Ripolin Blanc de Neige Can HP002



in-phase methylene twist

δ (CH_2)

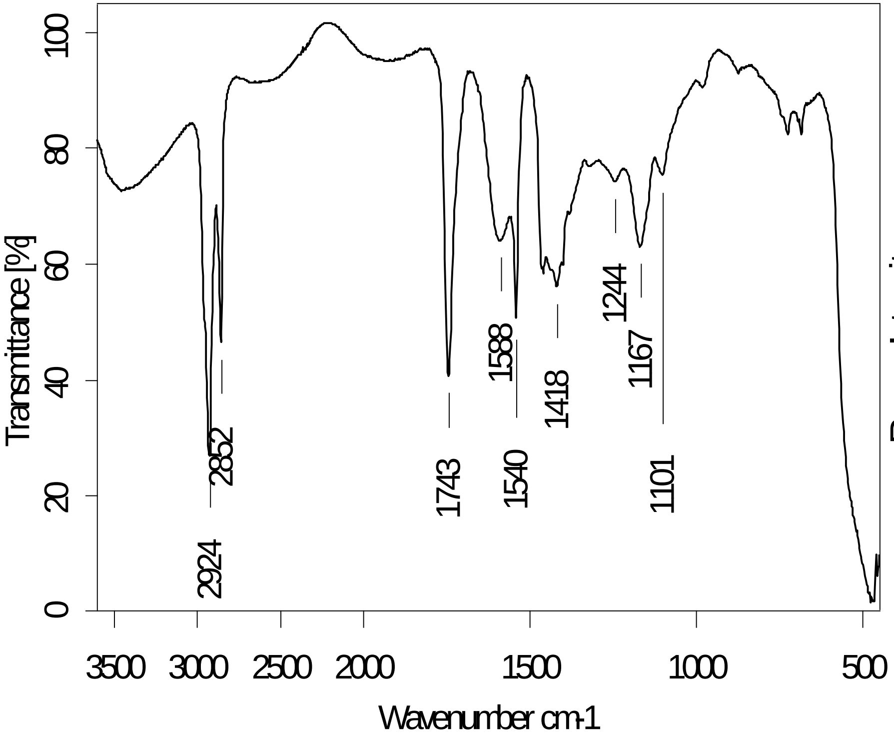
ν (C=C) isolated cis

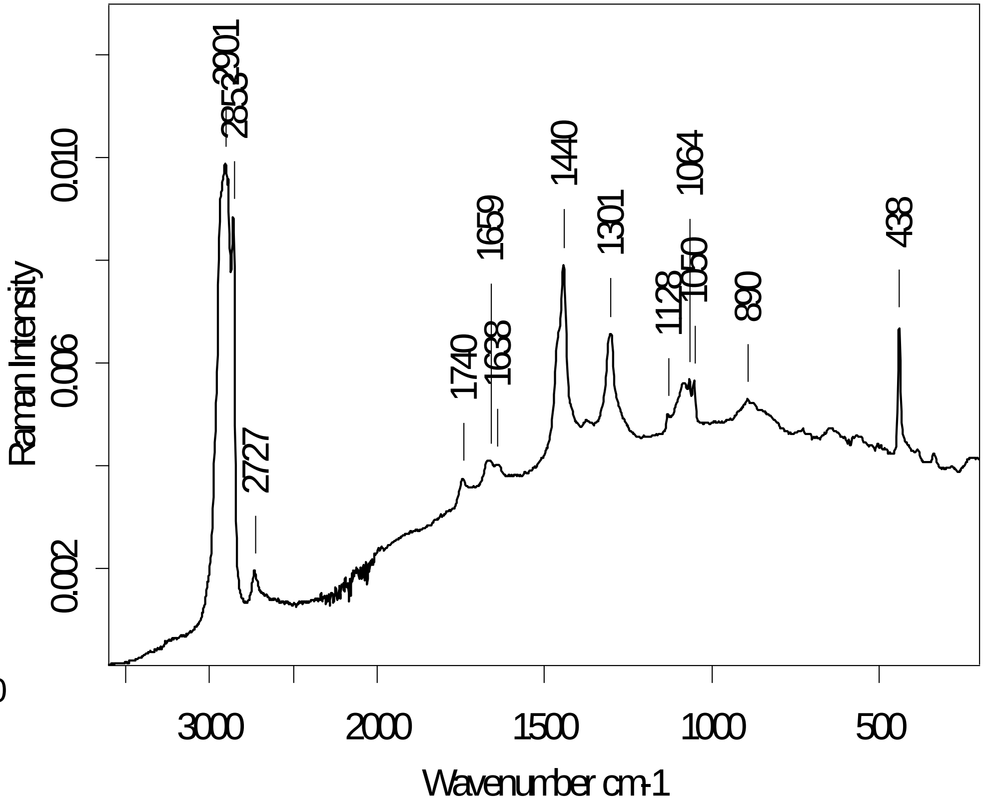
ν (CO); ν (C-C)

ZnO

FT-Raman, 100 mW avg of 20 spectra at 2000 scans each

LEFRANC artists’ zinc white tube paint (2007.48)

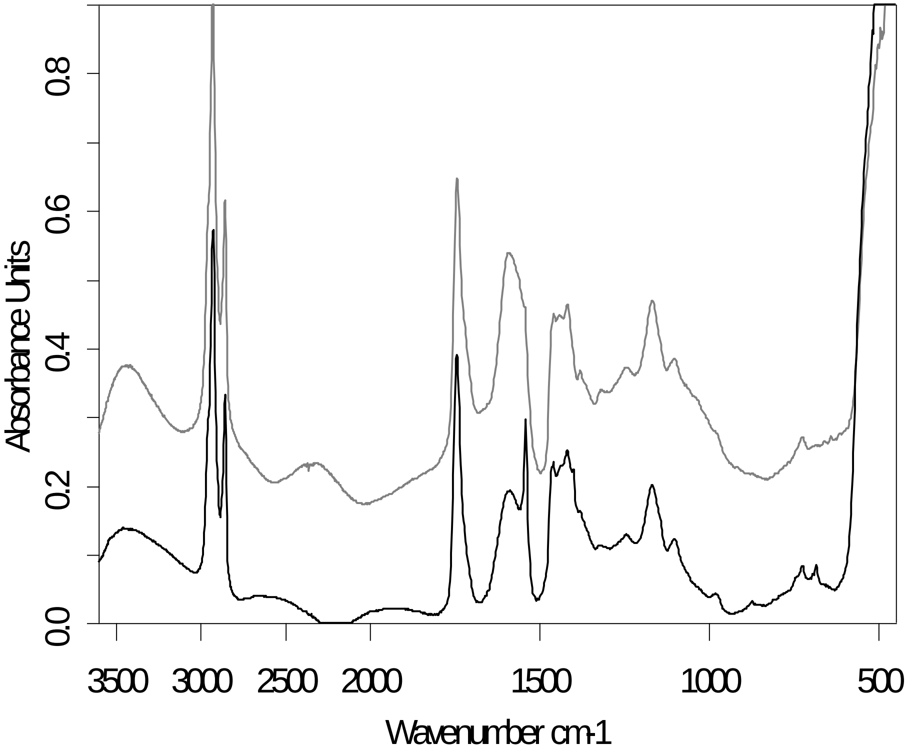


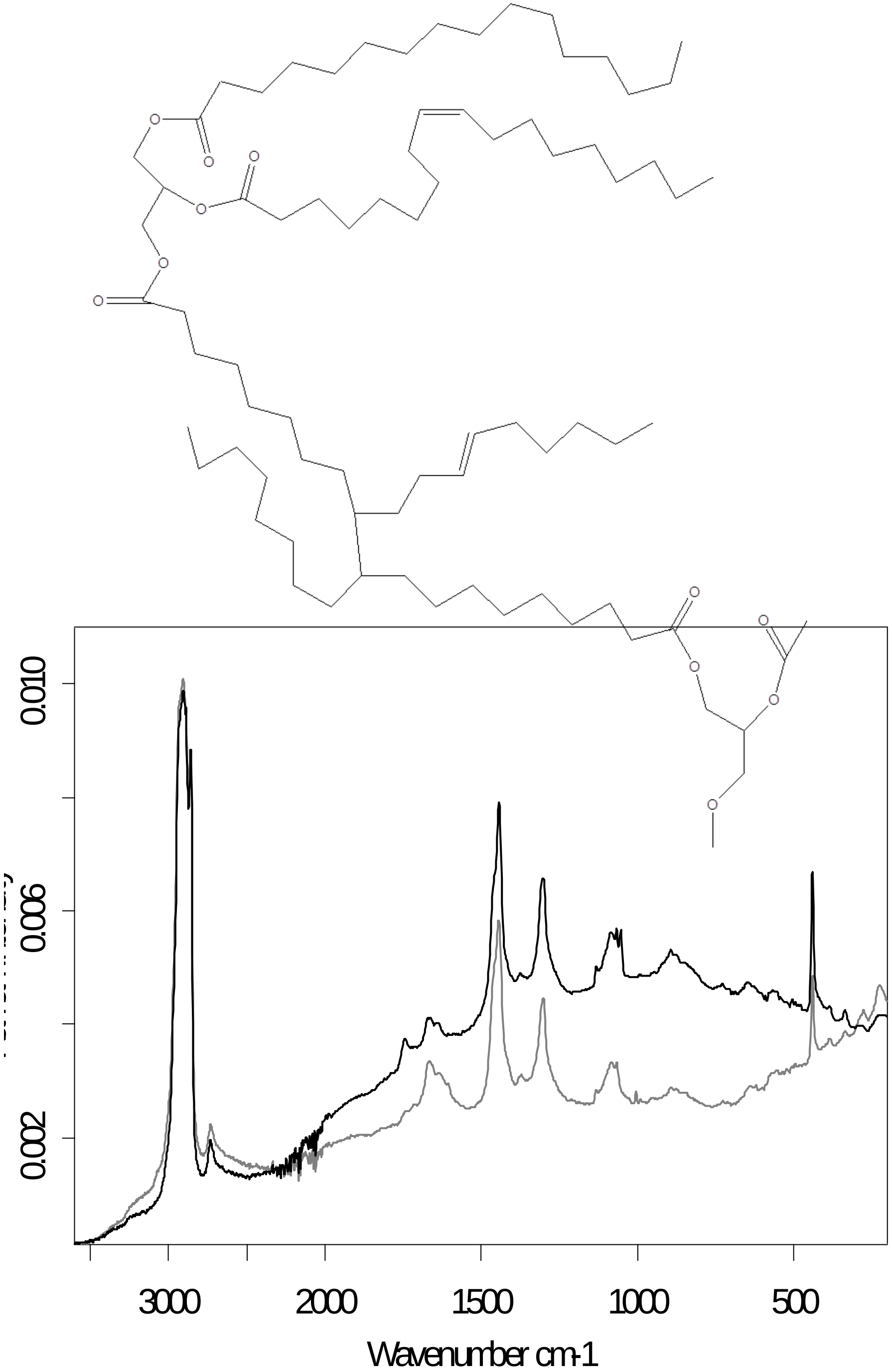


FT-Raman, 100 mW avg of 20 spectra at 2000 scans each

Ripolin Blanc de Neige
Can HP002

LEFRANC tube paint (2007.48)





FT/ DISPERSIVE - RAMAN/ FTIR of COLORANTS IN MODERN RESINS

***“Tuttomondo ”* (1989) Wall painting by Keith Haring (1958-1990), Pisa, Italy**

ART INSTITVTE CHICAGO

Regione Toscana

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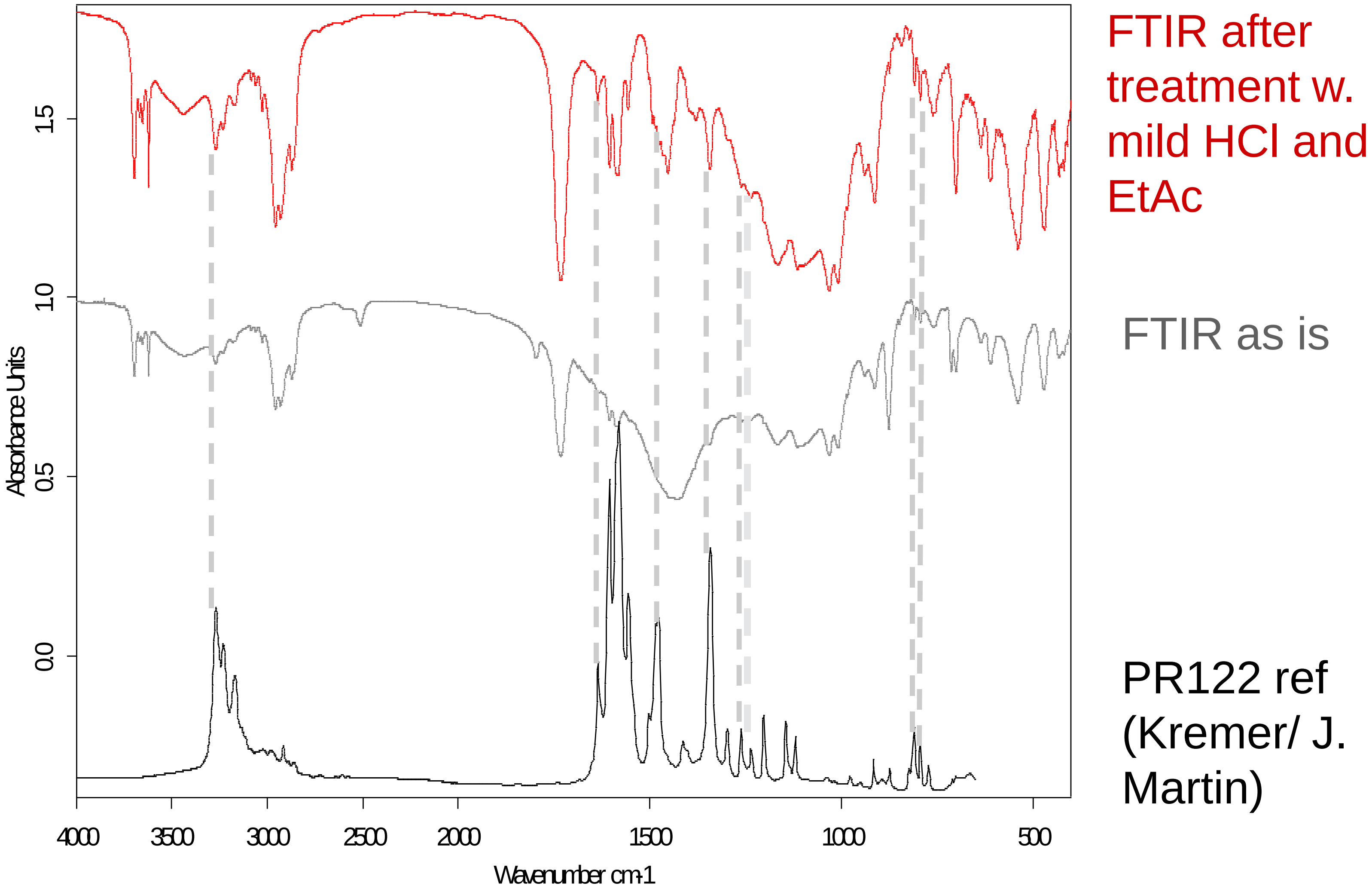
2007-2013

REPUBBLICA ITALIANA

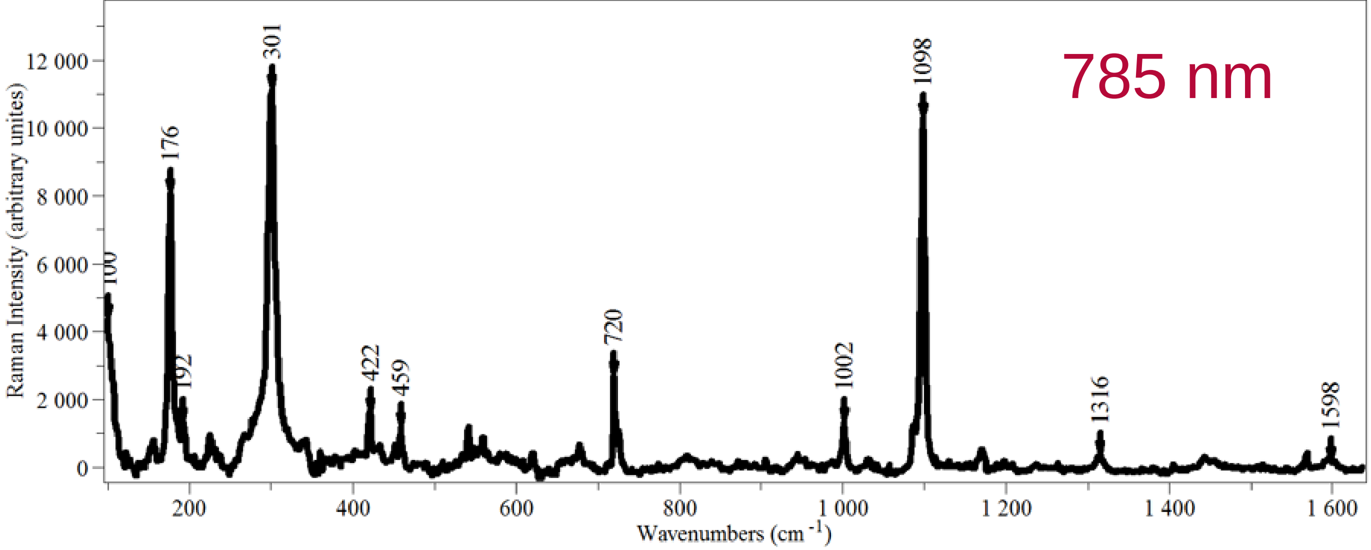
Marcello Picollo, Giovanni Bartolozzi, Marco De Vita

IFAC-CNR

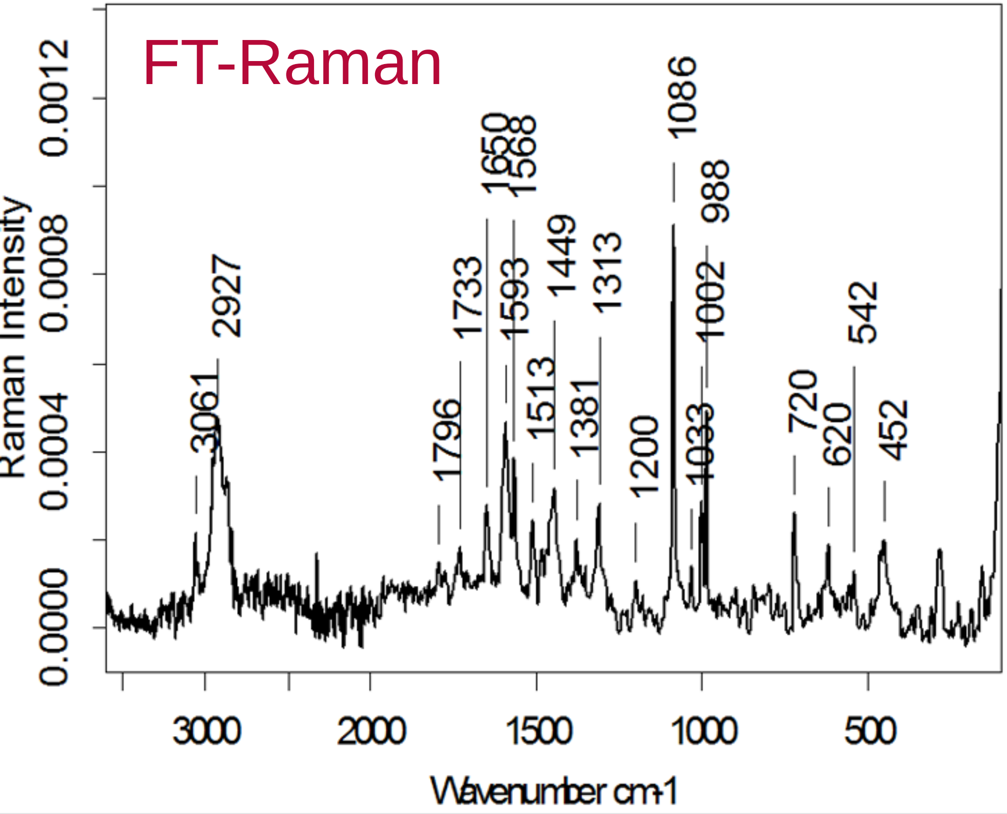


Colorant identified as PR122 (quinacridone)

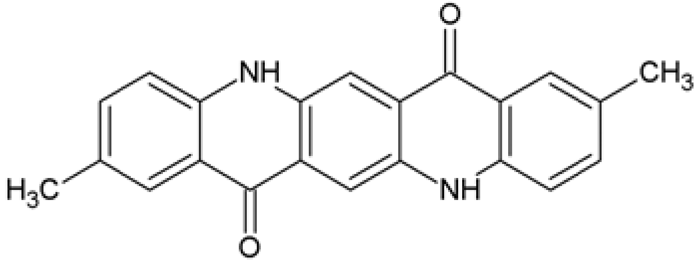
HARING 1R



Paint film as is



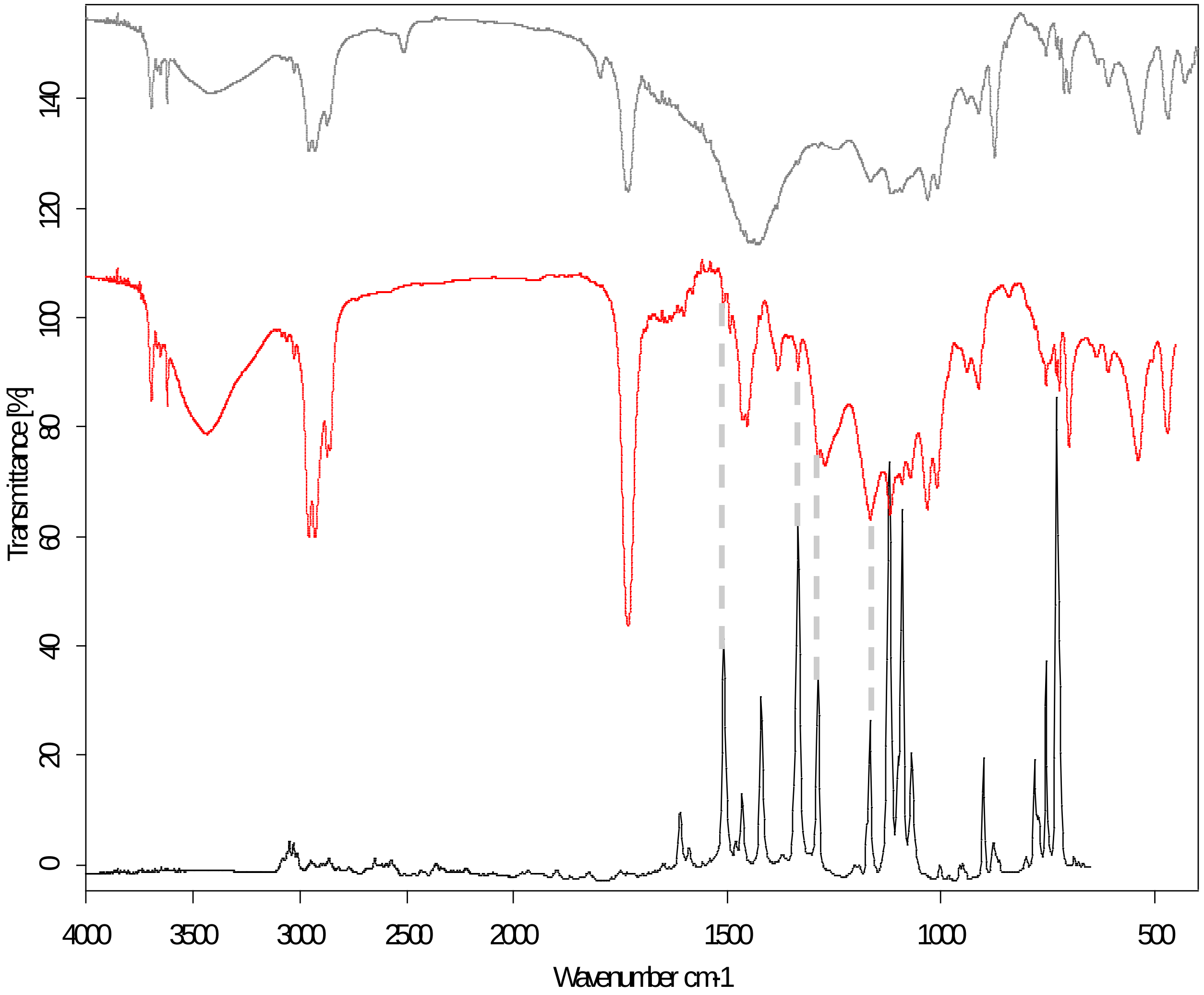
PR122: **1649s**; **1597s**; **1568vs**; **1512**; 1432; **1311s**; **460m**; 309; 233m



BaSO4 (453m, 988vs), calcite (282w, 1088vs),

Scherrer, N.C. et al., 2009. Synthetic organic pigments of the 20th and 21st century relevant to artist’s paints: Raman spectra reference collection. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 73(3):505–524

HARING BLUE



FTIR as is

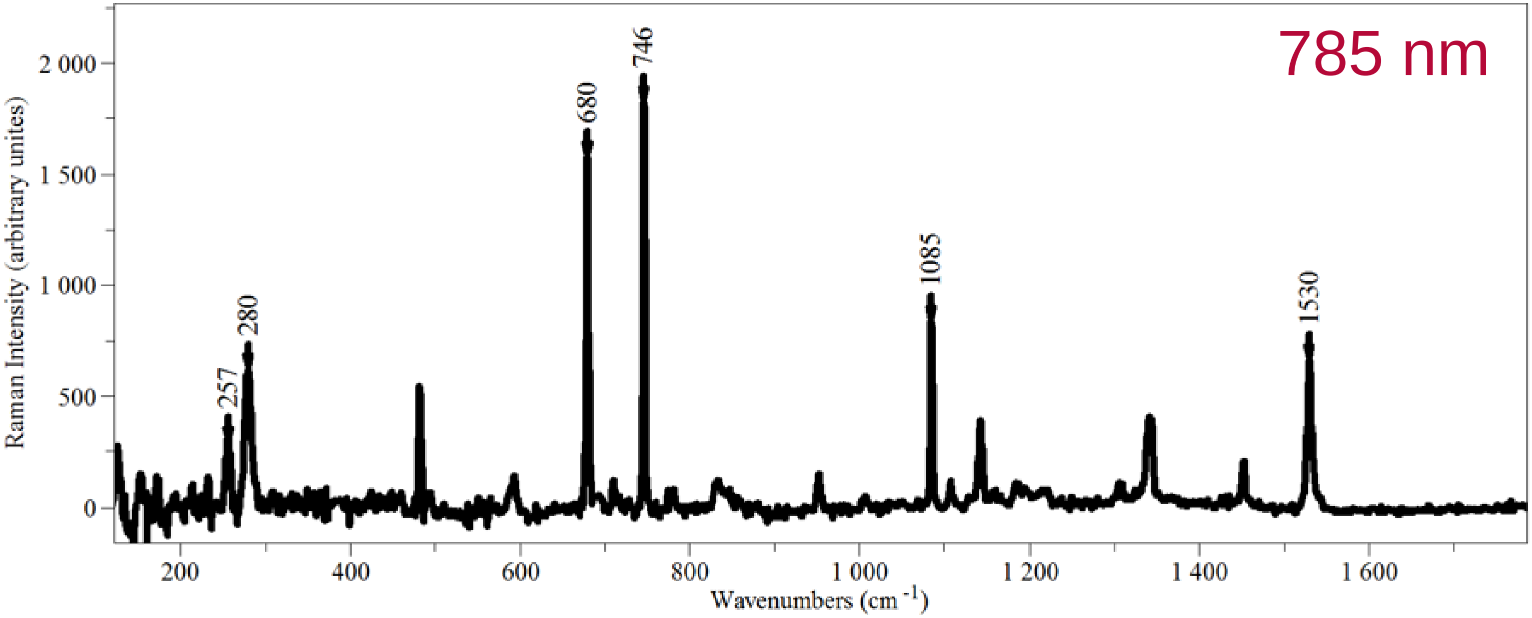
FTIR after treatment w. mild HCl and EtAc

PB 15:3 ref (Magruder/ J. Martin)

Colorant identified as PB 15:3 (phthalocyanine)

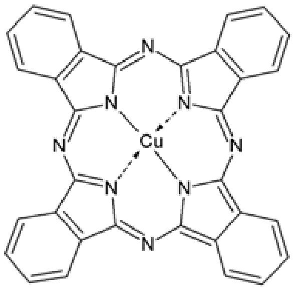
PB15:3 CI 74160:3

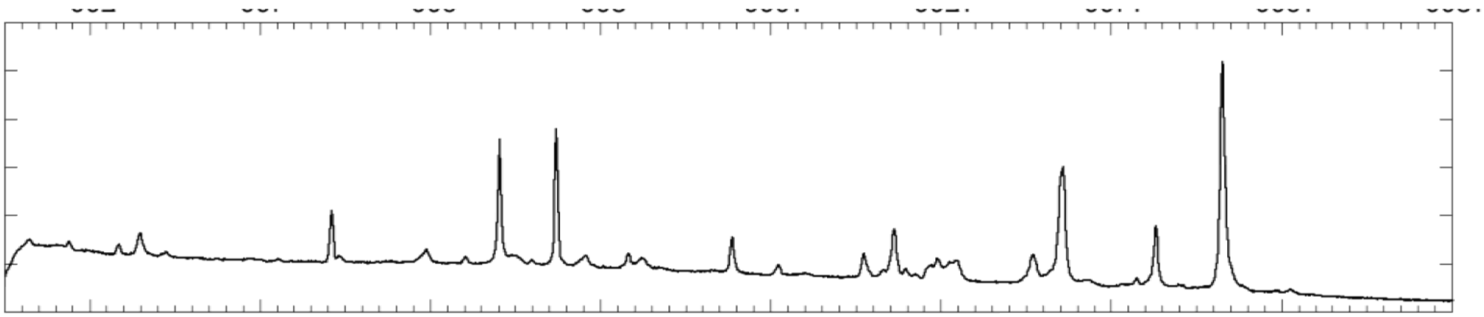
HARING BLUE



785 nm

FT-Raman: no spectrum





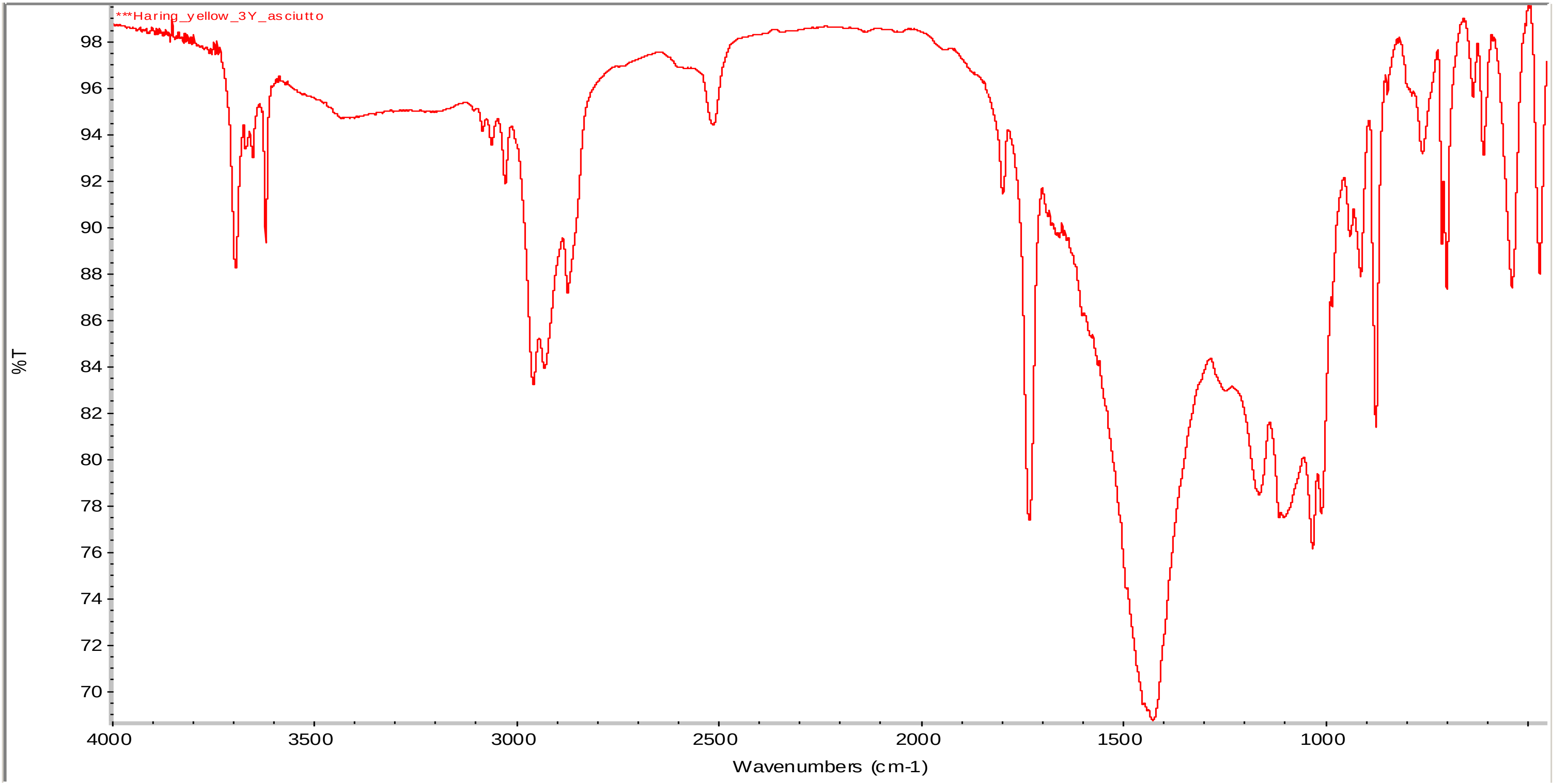
1530vs; 1451m; 1429; 1341s; 1307; 954; 747s; 681s; 483m; 289; 258

XRF identifies Ca, Ba, Cu, little Fe, Sr

BaSO4, calcite

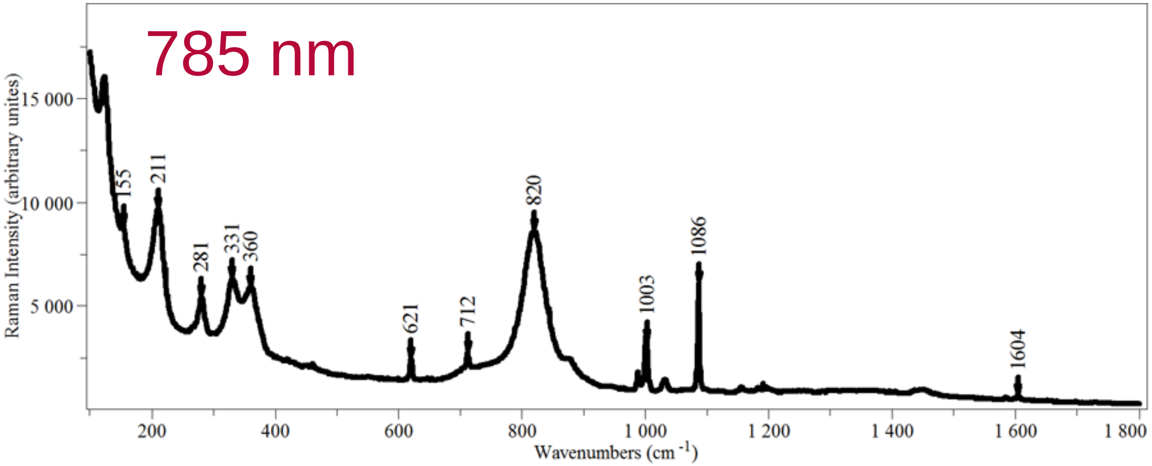
Scherrer, N.C. et al., 2009. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 73(3):505–524

HARING YELLOW



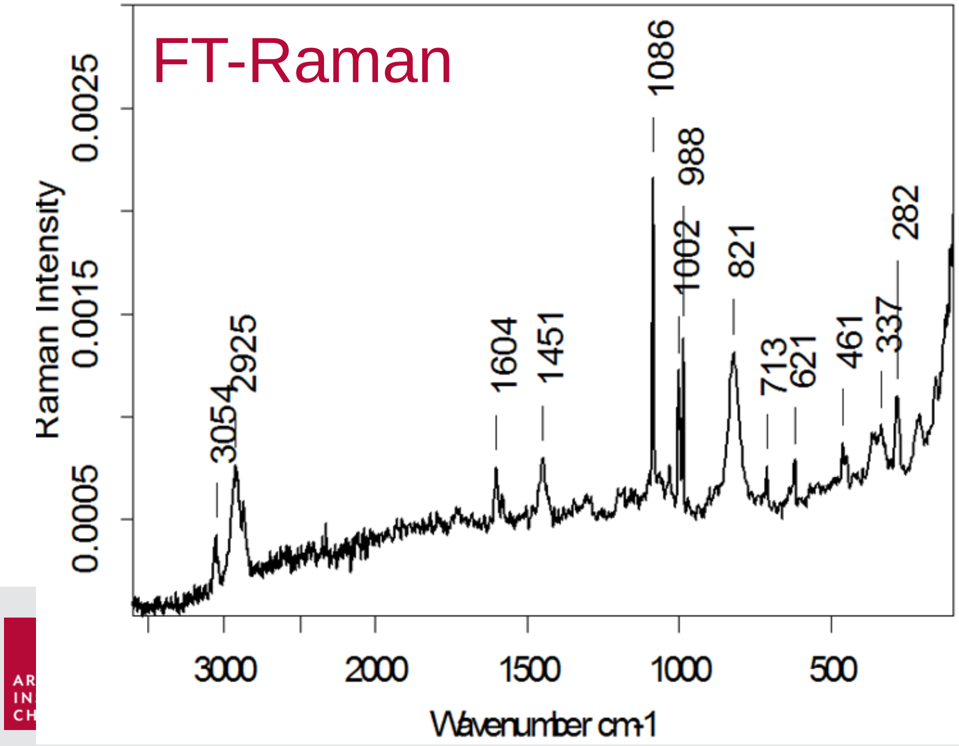
FTIR as is: no pigment ID possible

HARING YELLOW



Bismuth vanadate (PY184)

Clinobisvanite: $BiVO_4$

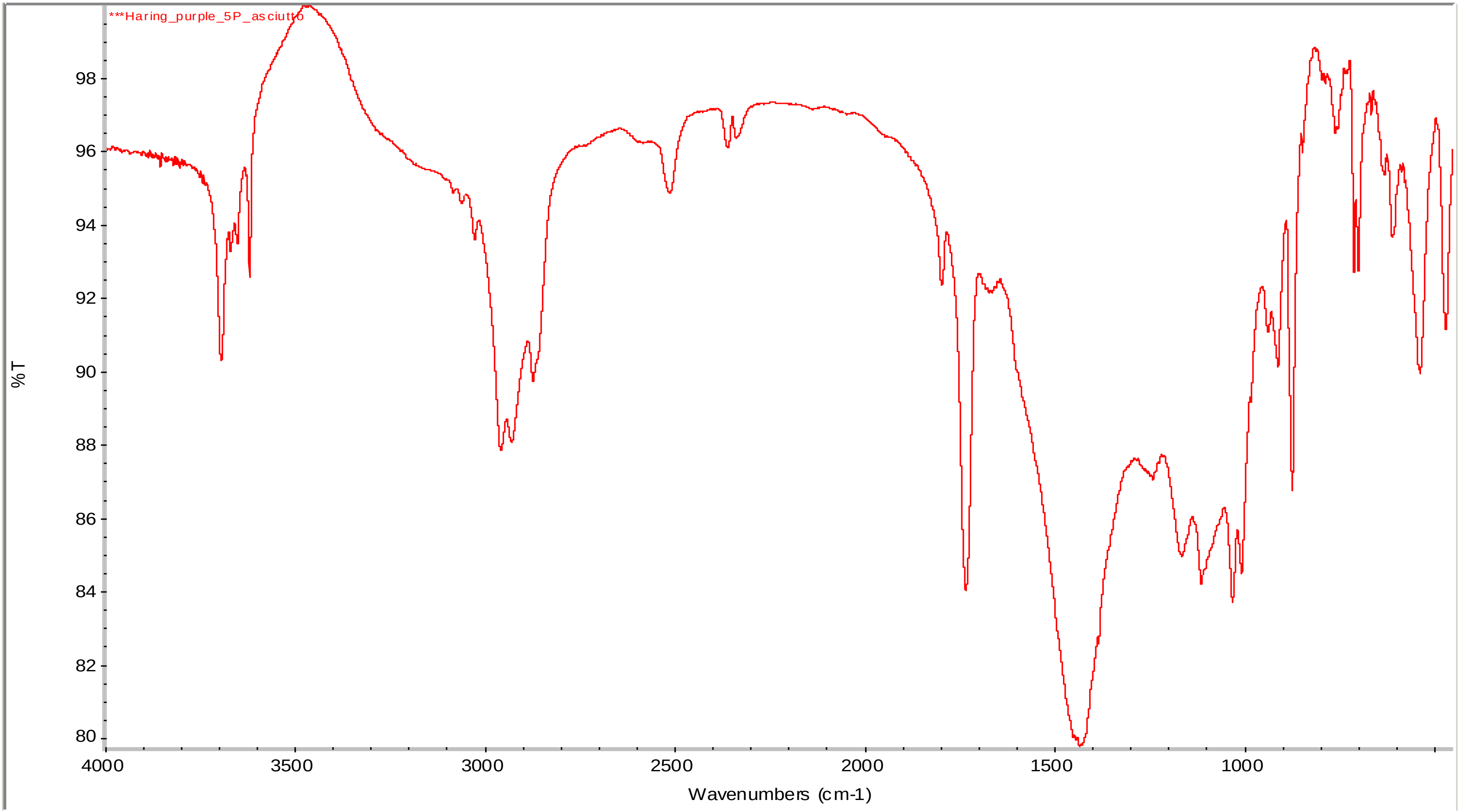


XRF identifies Bi, Ba, Sr, Ca, V, little Fe (V partly overlaps w. Ba Lα, so id ambiguous w. XRF only)

BaSO4, calcite, acrylic, resin

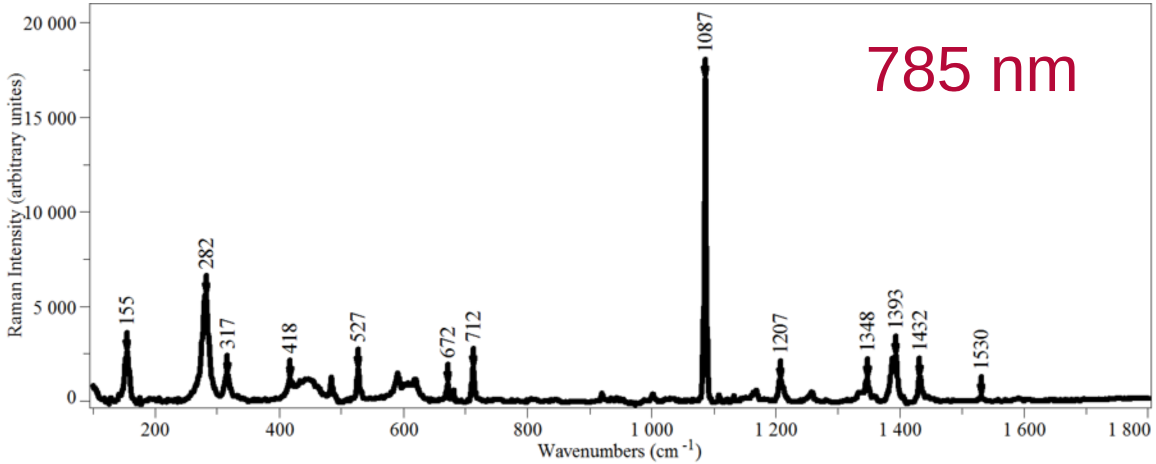
Frost, Ray and Henry, Dermot and Weier, Matt and Martens, Wayde (2006) Raman spectroscopy of three polymorphs of BiVO4: clinobisvanite, dreyerite and pucherite, with comparisons to (VO4)3-bearing-minerals: namibite, pottsite and schumacherite. Journal of Raman Spectroscopy 37(7):pp. 722-732

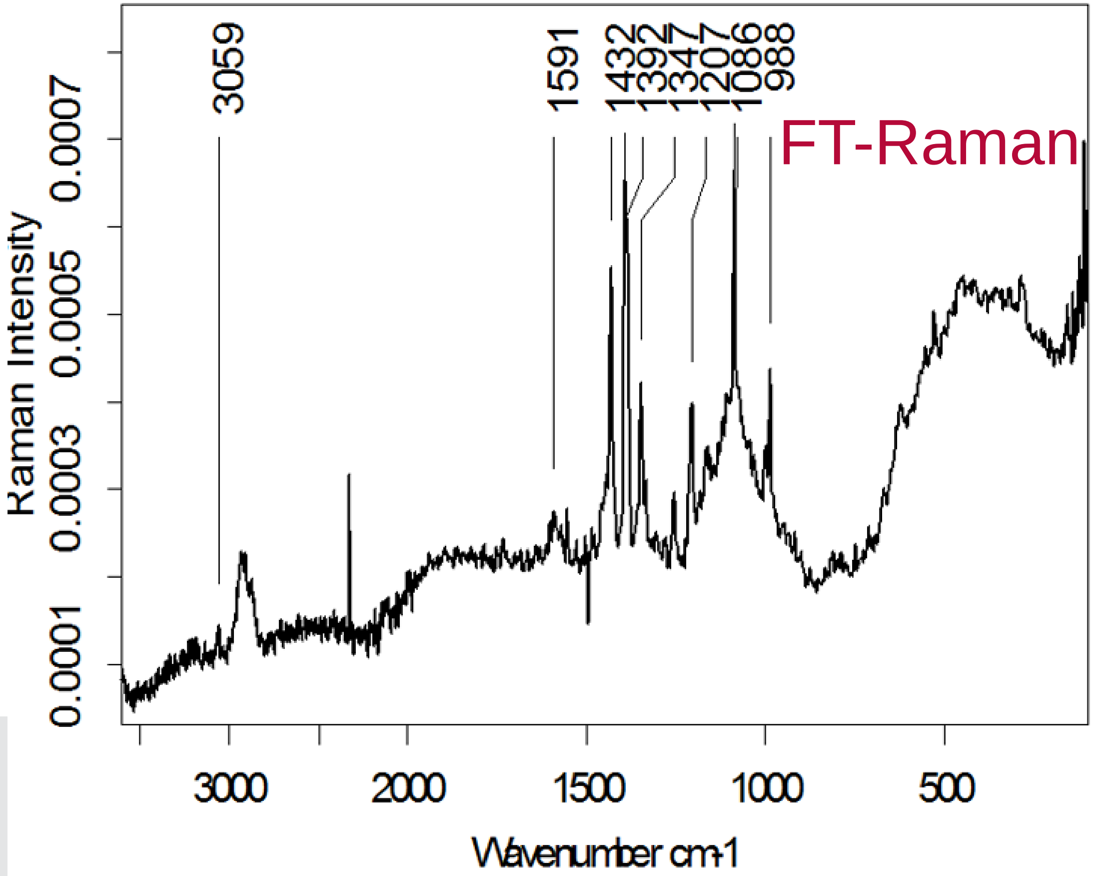
HARING PURPLE



FTIR as is: no pigment ID possible

HARING 5P PURPLE

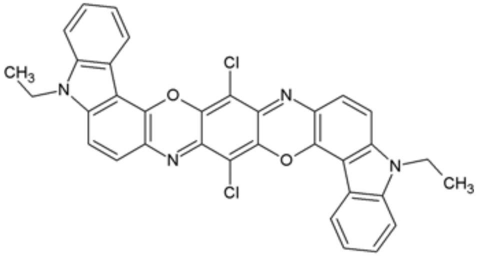




PV23 CI 51319

MONOLITE Violet RN

Heubach, Polycyclic pigment



1431m; 1391vs;

1347m; 1208m;

BaSO4, calcite

Scherrer, N.C. et al., 2009. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 73(3):505–524

- Acknowledgements:
- Regione Toscana (Tuscany, Italy) for having financed the Preventive Conservation of Contemporary Art (COPAC, 2011-2013) Project in the framework of PAR-FAS Regional Project (2007-13).
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- Fondazione Keith Haring
- Caparol Italy GmbH & Co
- Istituto di fisica Applicata Nello Carrara del CNR– Firenze (IFAC-CNR): Marcello Picollo, Costanza Cucci, Giovanni Bartolozzi, Veronica Marchiafava, Marco De Vita.
- Istituto di Chimica dei Composti Organo Metallici, Area di Ricerca CNR di Firenze (ICCOM-CNR): Vincenzo Palleschi, Stefano Legnaioli, Giulia Lorenzetti, Luciano Marras;
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- Oscar Chiantore (Università di Torino), Chiara Riedo (Università di Torino);
- Scuola Normale Superiore di Pisa: Vincenzo Barone, Franco Maria Nardini, Daniele Carta.
- Antonio Rava, Will Shank (restauratori)

Regione Toscana

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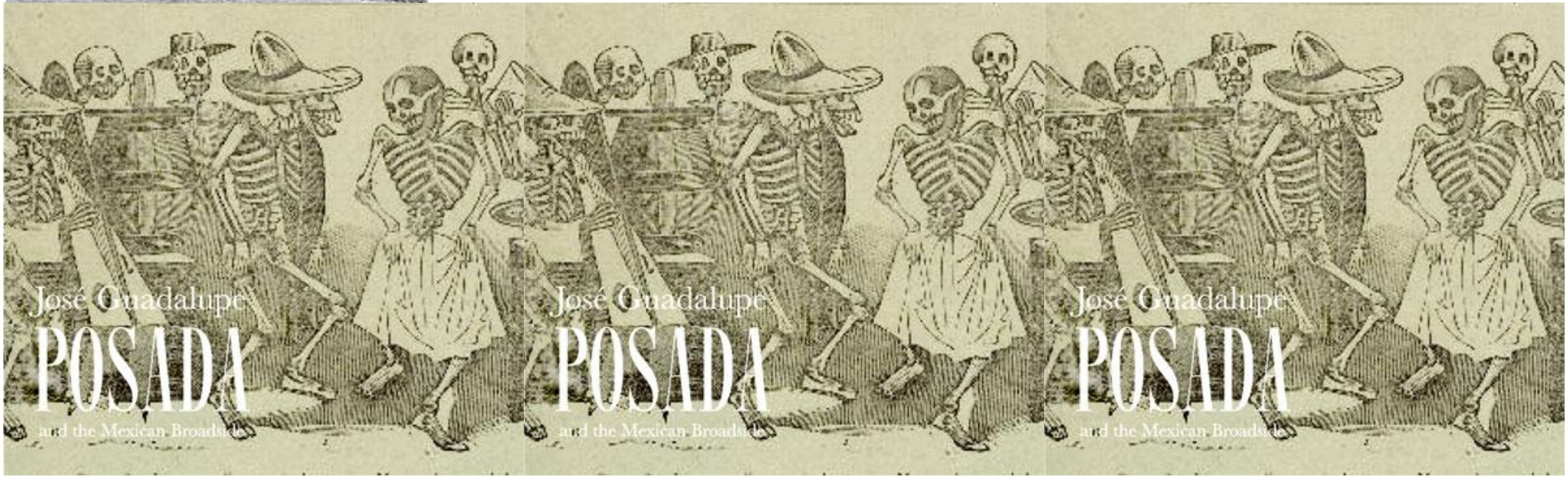
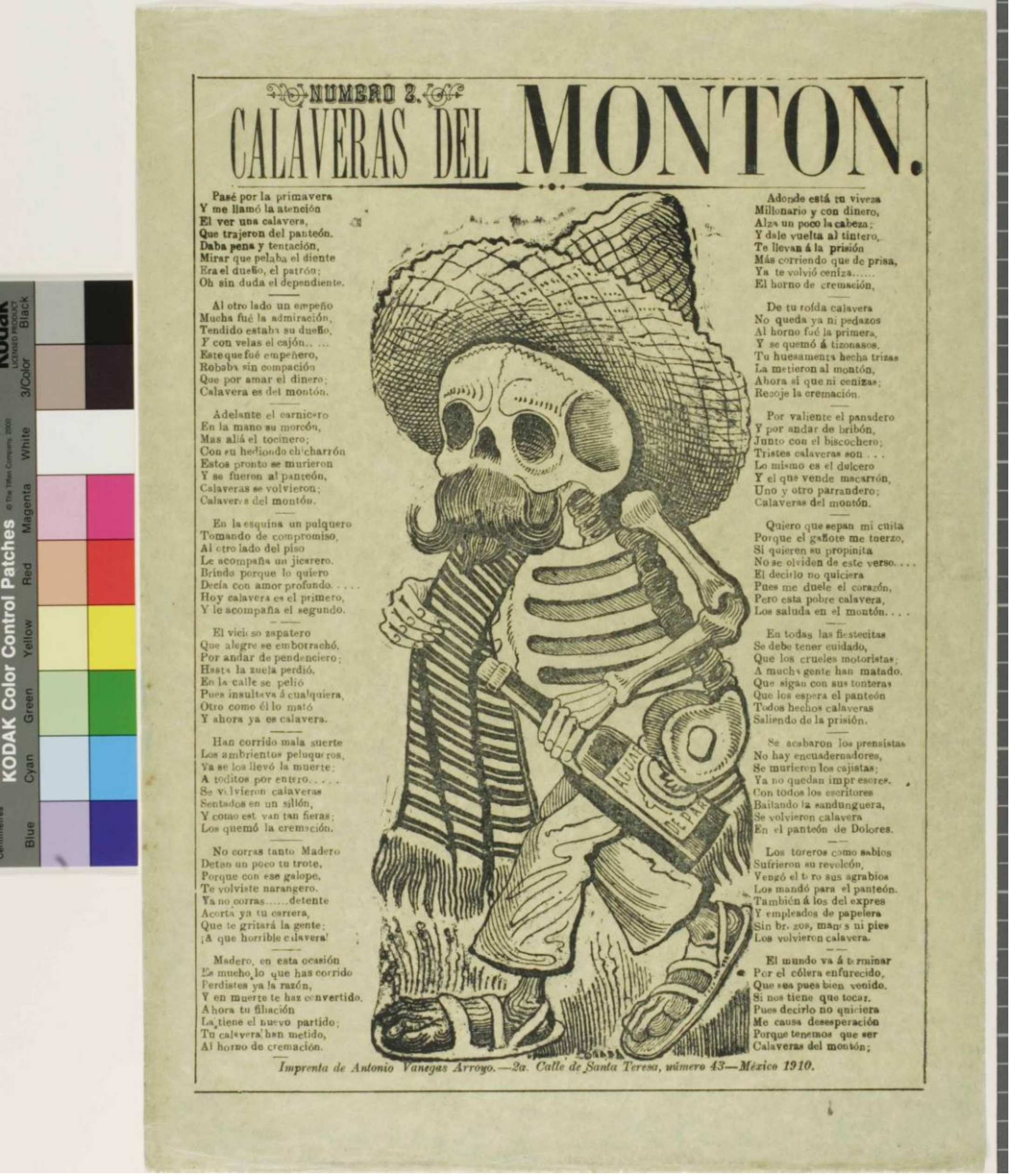
2007-2013

REPUBBLICA ITALIANA

DIRECT IDENTIFICATION OF EARLY SYNTHETIC ORGANIC DYES ON PAPER FIBERS : FT/ DISPERSIVE RAMAN STUDY





NUMERO 2.

CALAVERAS DEL MONTON.

Pasé por la primavera
Y me llamó la atención
El ver una calavera,
Que trajeron del panteón.
Daba pena y tentación,
Mirar que pelaba el diente
Era el dueño, el patrón;
Oh sin duda el dependiente.

Al otro lado un empeño
Mucha fué la admiración,
Tendido estaba su dueño,
Y con velas el cajón.. ...
Este que fué empeñero,
Robaba sin compación
Que por amar el dinero;
Calavera es del montón.

Adelante el carnicero
En la mano su morcón,
Mas allá el tocinero;
Con su hediondo chicharrón
Estos pronto se murieron
Y se fueron al panteón,
Calaveras se volvieron;
Calaveras del montón.

En la esquina un pulquero
Tomando de compromiso,
Al otro lado del piso
Le acompaña un jicarero.
Brindo porque lo quiero
Decía con amor profundo. . . . .
Hoy calavera es el primero,
Y le acompaña el segundo.

El vicioso zapatero
Que alegre se emborrachó,
Por andar de pendenciero;
Hasta la zuela perdió.
En la calle se pelió
Pues insultaba á cualquiera,
Otro como él lo mató
Y ahora ya es calavera.

Han corrido mala suerte
Los ambrientos peluqueros,
Ya se los llevó la muerte;
A toditos por entero. . . . .
Se volvieron calaveras
Sentados en un sillón,
Y como estaban tan fieras;
Los quemó la cremación.

No corras tanto Madero
Deten un poco tu trote,
Porque con ese galope,
Te volviste narangero.
Ya no corras......detente
Acorta ya tu carrera,
Que te gritará la gente;
¡A que horrible calavera!

Madero, en esta ocasión
Es mucho lo que has corrido
Perdistes ya la razón,
Y en muerte te haz convertido.
Ahora tu filiación
La tiene el nuevo partido;
Tu calavera han metido,
Al horno de cremación.

Adonde está tu viveza
Millonario y con dinero,
Alza un poco la cabeza;
Y dale vuelta al tintero,
Te llevan á la prisión
Más corriendo que de prisa,
Ya te volvió ceniza......
El horno de cremación,

De tu roída calavera
No queda ya ni pedazos
Al horno fué la primera,
Y se quemó á tizonasos.
Tu huesamenta hecha trizas
La metieron al montón,
Ahora sí que ni cenizas;
Recoje la cremación.

Por valiente el panadero
Y por andar de bribón,
Junto con el biscochero;
Tristes calaveras son . . .
Lo mismo es el dulcero
Y el que vende macarrón,
Uno y otro parrandero;
Calaveras del montón.

Quiero que sepan mi cuita
Porque el gañote me tuerzo,
Si quieren su propinita
No se olviden de este verso. . . .
El decirlo no quiciera
Pues me duele el corazón,
Pero esta pobre calavera,
Los saluda en el montón. . . .

En todas las fiestecitas
Se debe tener cuidado,
Que los crueles motoristas;
A mucha gente han matado.
Que sigan con sus tonteras
Que los espera el panteón
Todos hechos calaveras
Saliendo de la prisión.

Se acabaron los prensistas
No hay encuadernadores,
Se murieron los cajistas;
Ya no quedan impresores.
Con todos los escritores
Bailando la sandunguera,
Se volvieron calavera
En el panteón de Dolores.

Los toreros como sabios
Sufrieron su revolcón,
Vengó el toro sus agrabios
Los mandó para el panteón.
También á los del expres
Y empleados de papelera
Sin brazos, manos ni pies
Los volvieron calavera.

El mundo va á terminar
Por el cólera enfurecido,
Que sea pues bien venido,
Si nos tiene que tocar.
Pues decirlo no quiciera
Me causa desesperación
Porque tenemos que ser
Calaveras del montón;

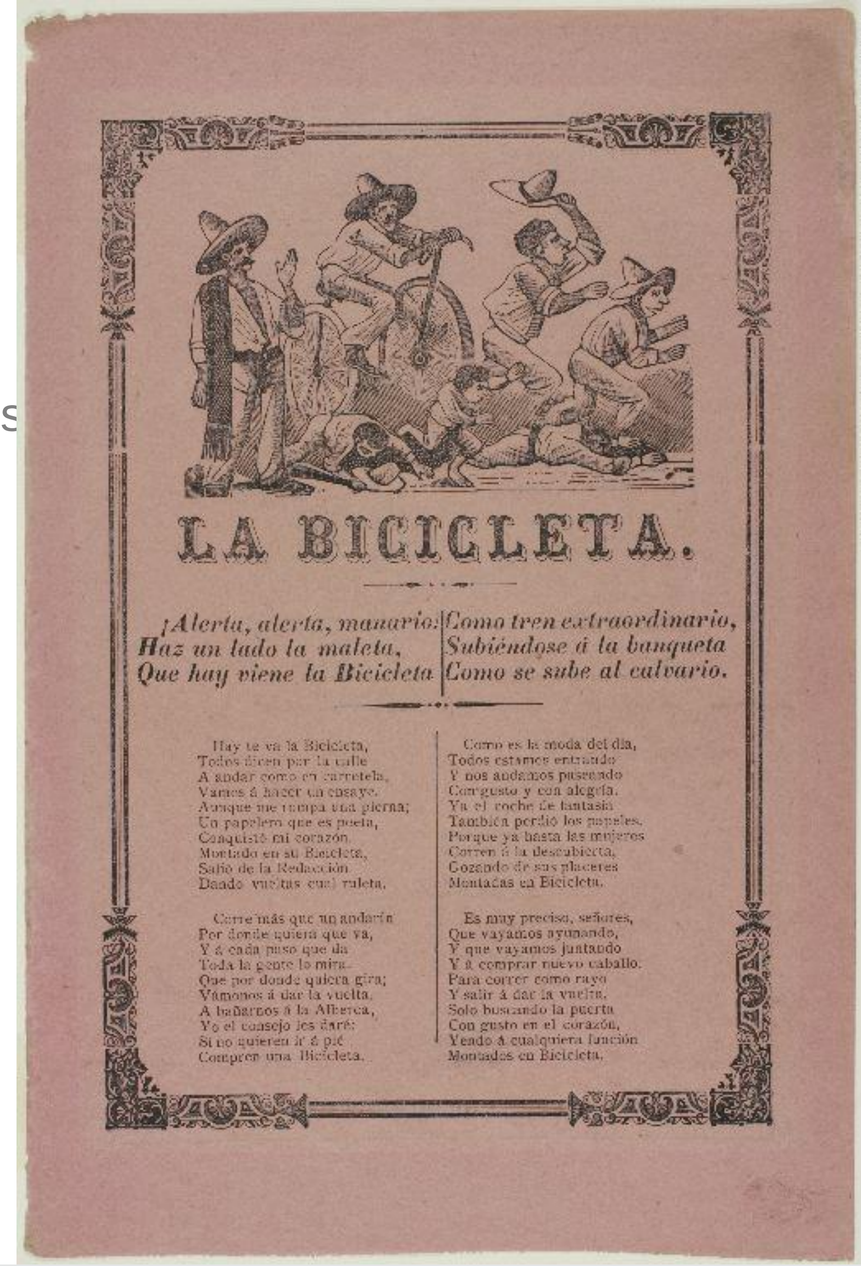
Imprenta de Antonio Vanegas Arroyo.—2a. Calle de Santa Teresa, número 43—México 1910.

Photo-relief etching

Calavera of Francisco Madero

Jose Guadalupe Posada collection

- Printed on colored papers
- Vivid colors visually matched to aniline dye manuals
- Fading
- Problems with moisture (aqueous treatments
high humidity environment)



LA BICICLETA.

¡Alerta, alerta, manario!
Haz un lado la maleta,
Que hay viene la Bicicleta
Como tren extraordinario,
Subiéndose á la banqueta
Como se sube al calvario.

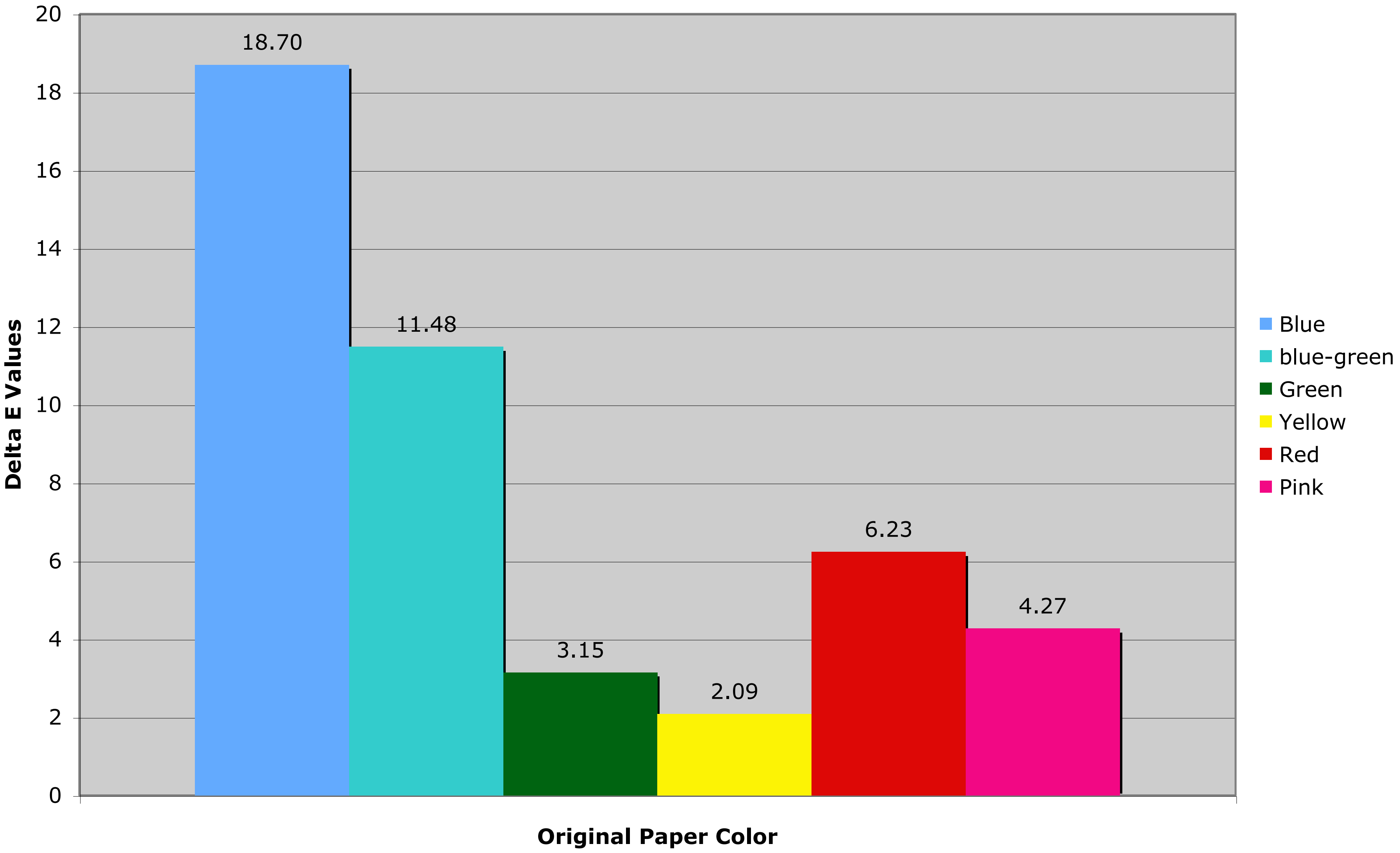
Hay te va la Bicicleta,
Todos dicen por la calle
A andar como en carretela,
Vamos á hacer un ensayo.
Aunque me rompa una pierna;
Un papelero que es poeta,
Conquistó mi corazón
Montado en su Bicicleta,
Salió de la Redacción
Dando vueltas cual ruleta.

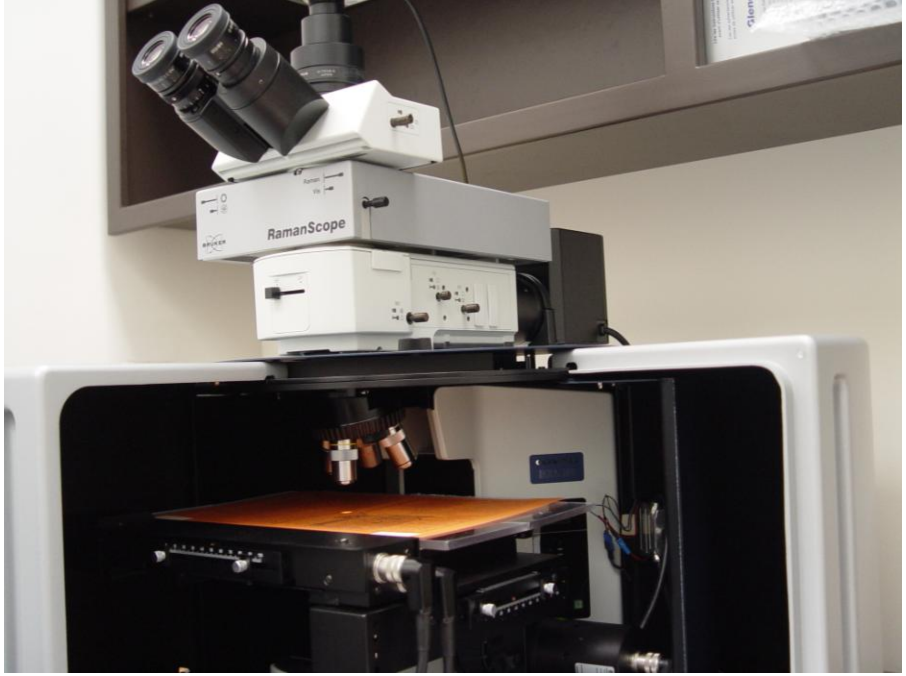
Corre más que un andarín
Por donde quiera que va,
Y á cada paso que da
Toda la gente lo mira.
Que por donde quiera gira;
Vámonos á dar la vuelta,
A bañarnos á la Alberca,
Yo el consejo les daré:
Si no quieren ir á pié
Compren una Bicicleta.

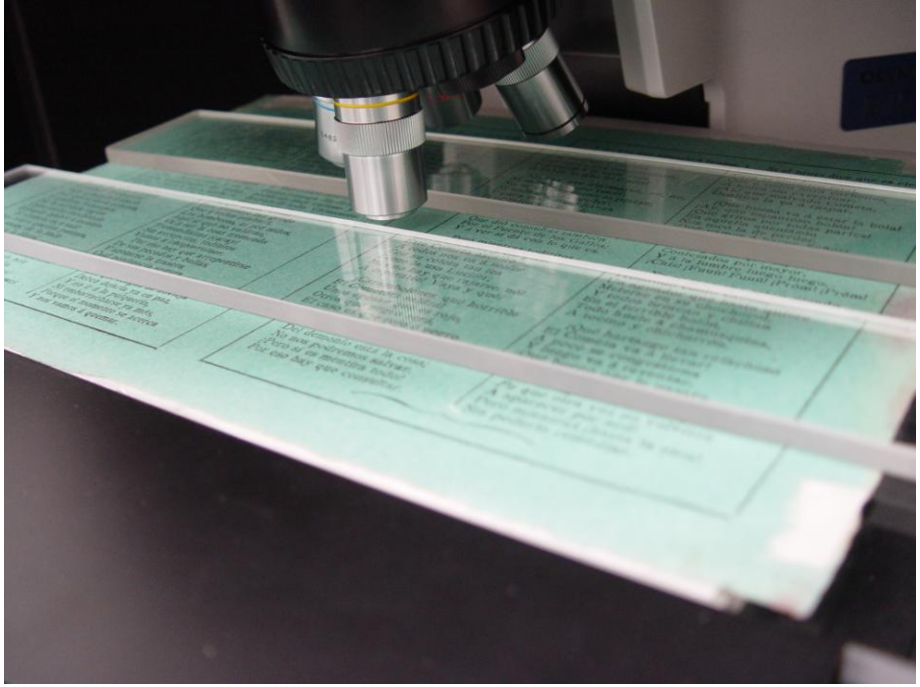
Como es la moda del dia,
Todos estamos entrando
Y nos andamos paseando
Con gusto y con alegría.
Ya el coche de fantasía
También perdió los papeles,
Porque ya hasta las mujeres
Corren á la descubierta,
Gozando de sus placeres
Montadas en Bicicleta.

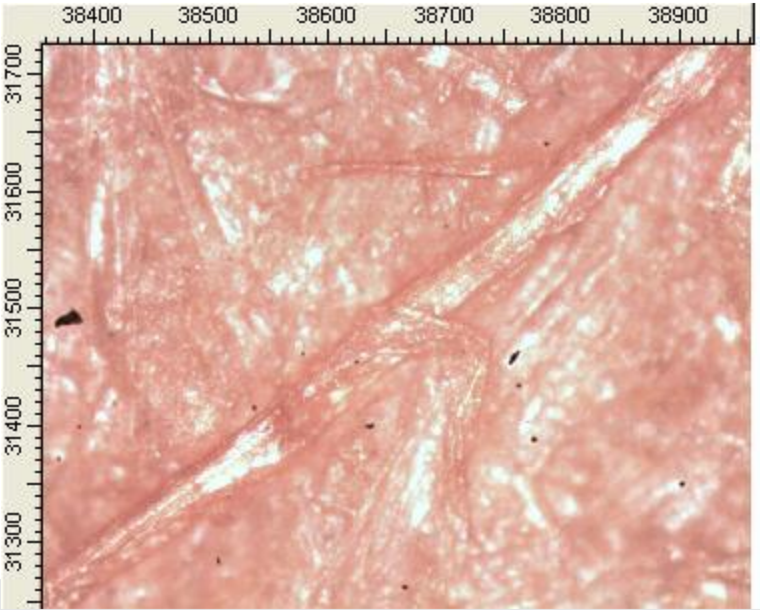
Es muy preciso, señores,
Que vayamos ayunando,
Y que vayamos juntando
Y á comprar nuevo caballo.
Para correr como rayo
Y salir á dar la vuelta,
Solo buscando la puerta
Con gusto en el corazón,
Yendo á cualquiera función
Montados en Bicicleta.

Color Loss Verso:Recto Before Exhibition









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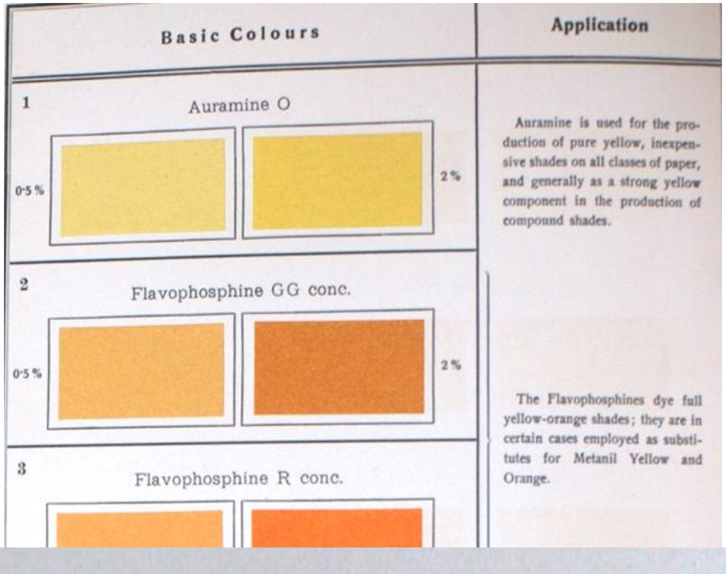
CHICAGO

F. Casadio, K. Mauck, M. Chefitz, R. Freeman Direct Identification Of Early Synthetic Organic Dyes: Ft-Raman Study Of The Illustrated Broadside Prints Of Jose' Guadalupe Posada (1852-1913), Applied Physics A, (2010) 100: 885-899

I.G. Farbenindusrie aktiengesellschaft. The dyeining of Paper in the Pulp, 1926



Basic Colours | **Application**

1 Auramine O

0·5 % 2 %

Auramine is used for the production of pure yellow, inexpensive shades on all classes of paper, and generally as a strong yellow component in the production of compound shades.

2 Flavophosphine GG conc.

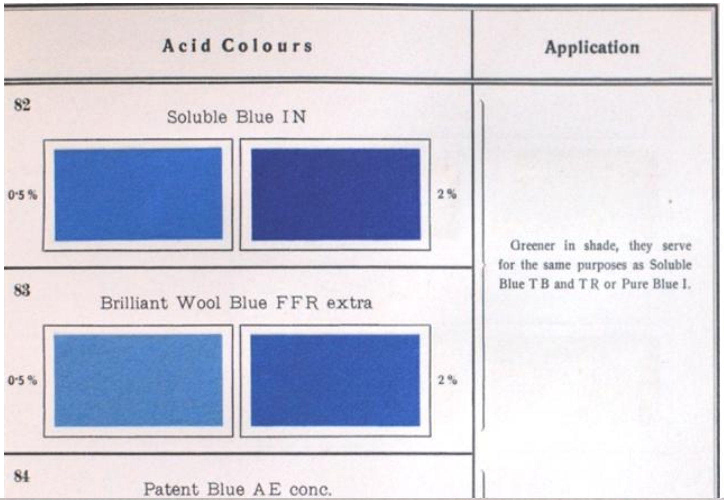
0·5 % 2 %

3 Flavophosphine R conc.

The Flavophosphines dye full yellow-orange shades; they are in certain cases employed as substitutes for Metanil Yellow and Orange.

0·5 % 2 %

See page 23.



Acid Colours | **Application**

82 Soluble Blue IN

0·5 % 2 %

83 Brilliant Wool Blue FFR extra

0·5 % 2 %

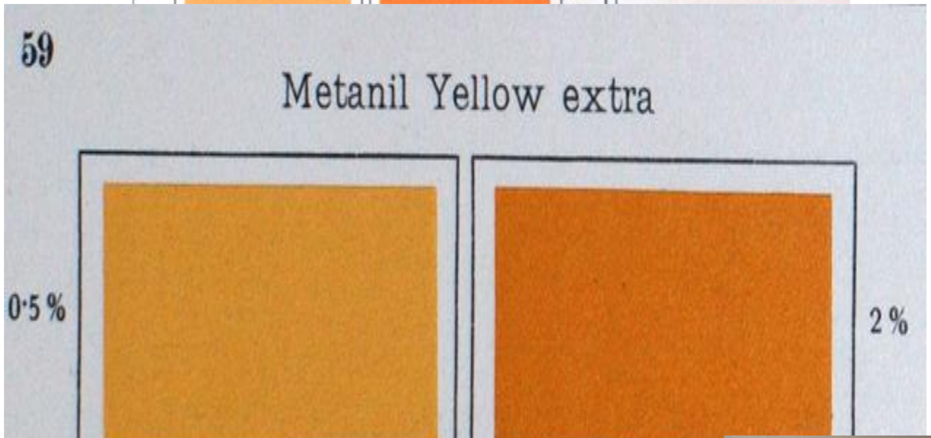
Greener in shade, they serve for the same purposes as Soluble Blue TB and TR or Pure Blue I.

84 Patent Blue AE conc.

Brilliant Acid Green 6B

2 %

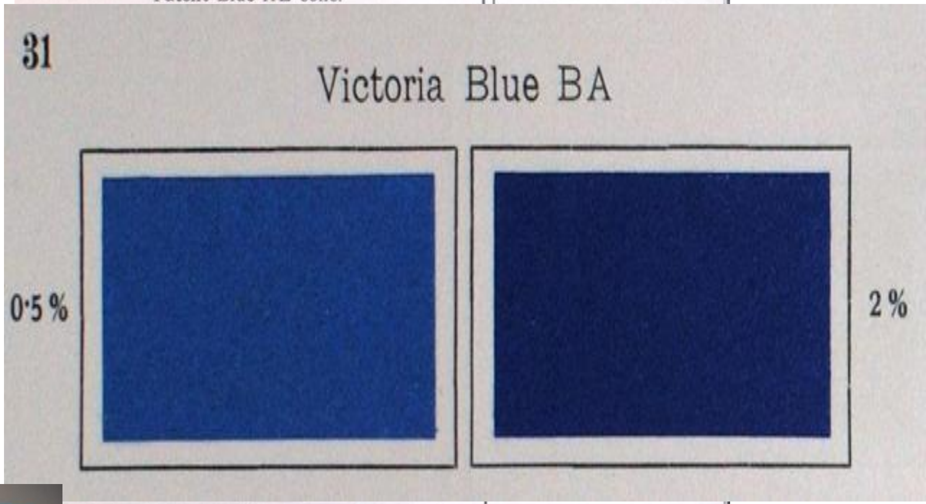
For the production on mixed pulps of uniform, bright green shades.



59

Metanil Yellow extra

0·5 % 2 %



31

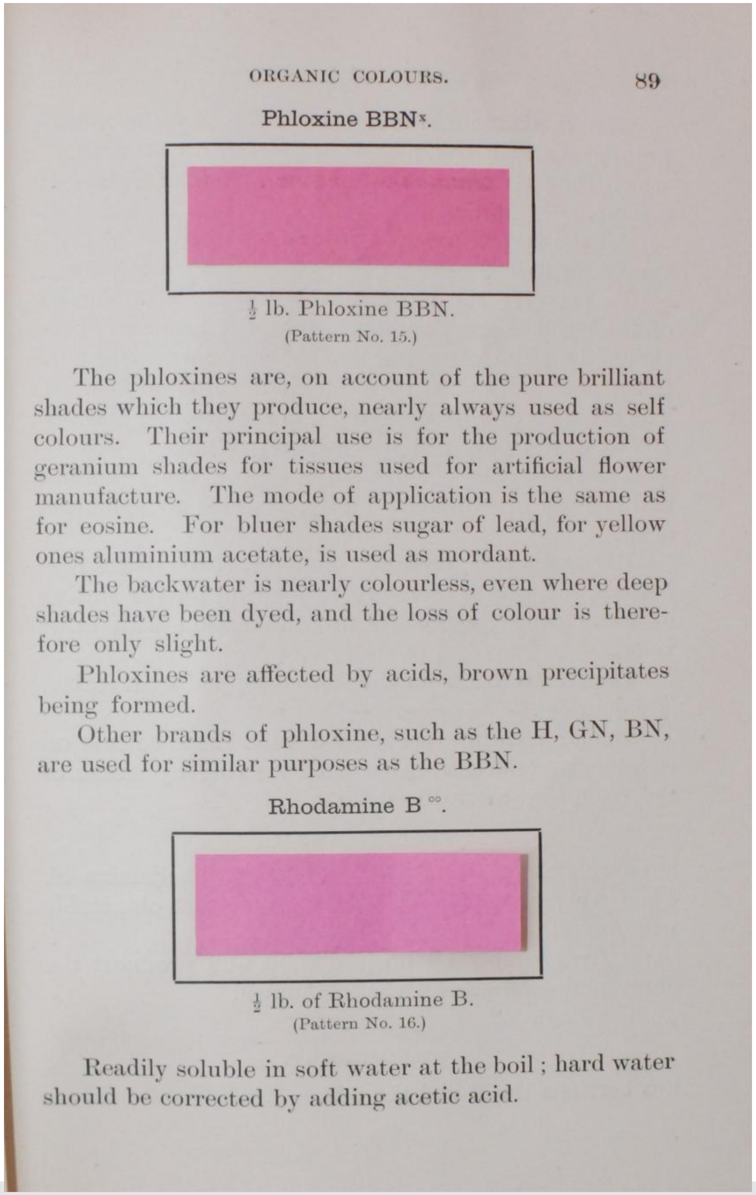
Victoria Blue BA

0·5 % 2 %

I.G. FARBENINDUSTRIE
AKTIENGESELLSCHAFT
FRANKFURT A. MAIN

The Dyeing of Paper in the Pulp

Erfurt



ORGANIC COLOURS. 89

Phloxine BBN˟.

½ lb. Phloxine BBN.
(Pattern No. 15.)

The phloxines are, on account of the pure brilliant shades which they produce, nearly always used as self colours. Their principal use is for the production of geranium shades for tissues used for artificial flower manufacture. The mode of application is the same as for eosine. For bluer shades sugar of lead, for yellow ones aluminium acetate, is used as mordant.

The backwater is nearly colourless, even where deep shades have been dyed, and the loss of colour is therefore only slight.

Phloxines are affected by acids, brown precipitates being formed.

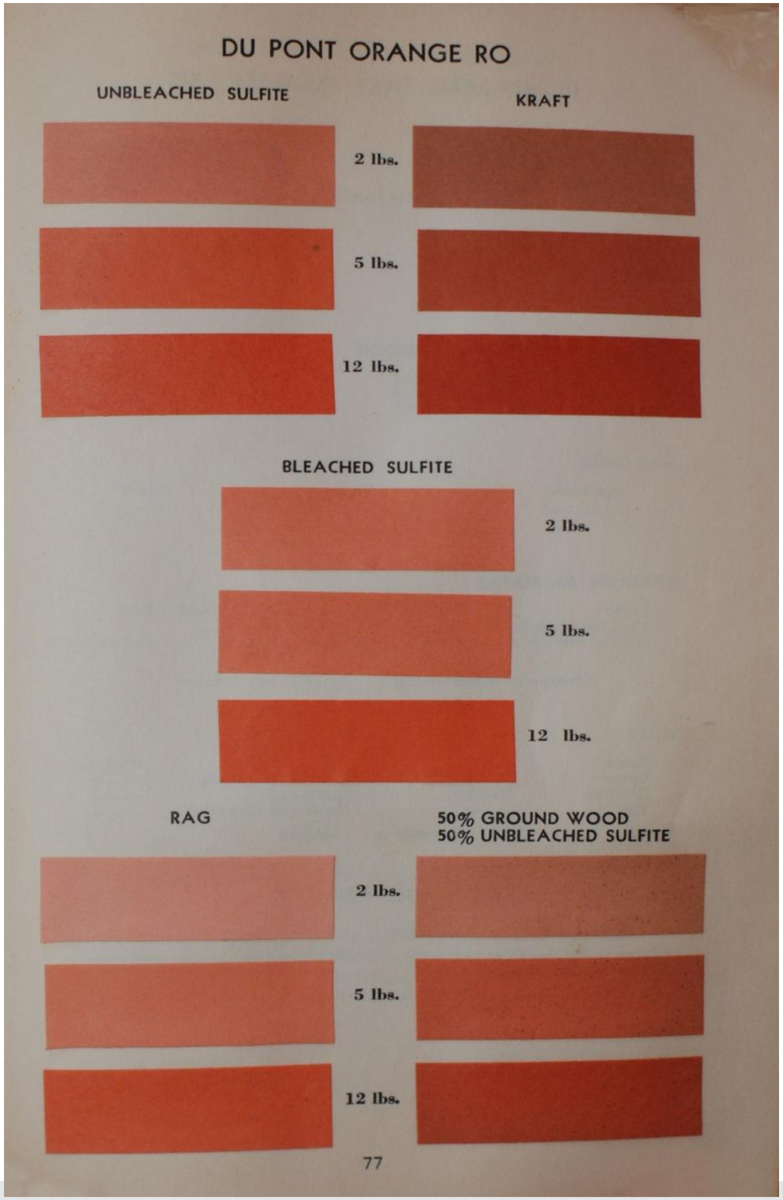
Other brands of phloxine, such as the H, GN, BN, are used for similar purposes as the BBN.

Rhodamine B ˚˚.

½ lb. of Rhodamine B.
(Pattern No. 16.)

Readily soluble in soft water at the boil; hard water should be corrected by adding acetic acid.

Du Pont



DU PONT ORANGE RO

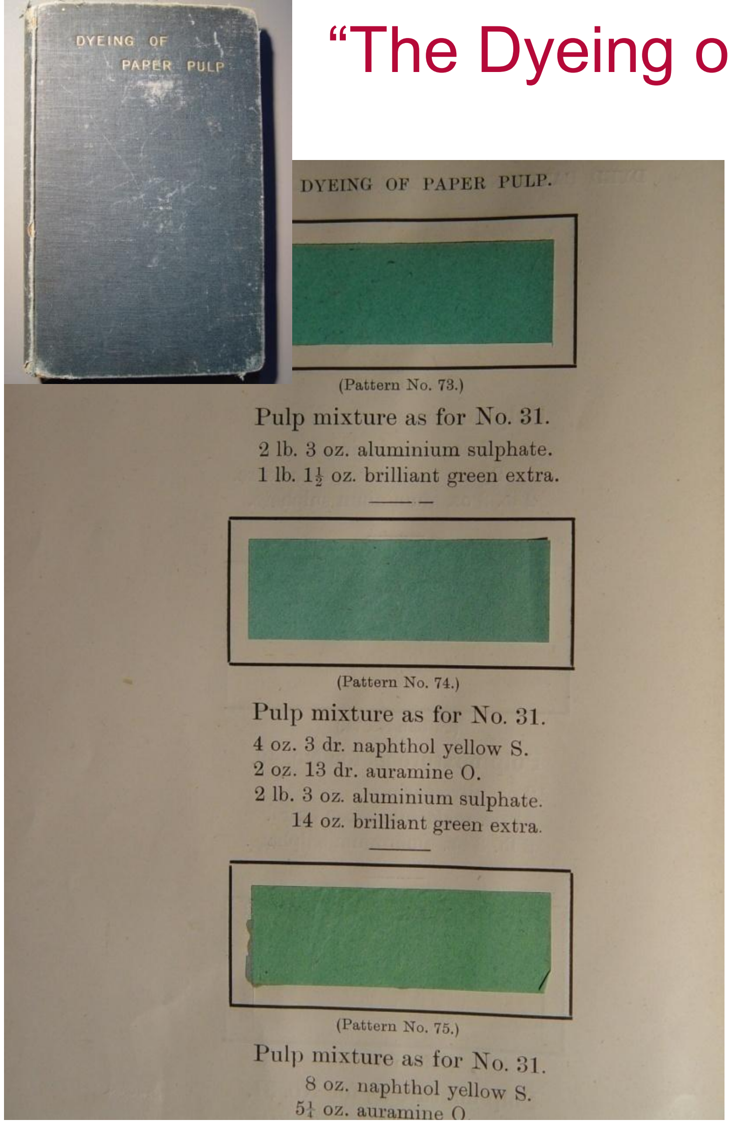
UNBLEACHED SULFITE		KRAFT
🟧	2 lbs.	🟧
🟧	5 lbs.	🟧
🟧	12 lbs.	🟧

BLEACHED SULFITE	
🟧	2 lbs.
🟧	5 lbs.
🟧	12 lbs.

RAG		50% GROUND WOOD 50% UNBLEACHED SULFITE
🟧	2 lbs.	🟧
🟧	5 lbs.	🟧
🟧	12 lbs.	🟧

77

“The Dyeing of Paper Pulp” by Julius Erfurt1901



DYEING OF PAPER PULP.

(Pattern No. 73.)

Pulp mixture as for No. 31.

2 lb. 3 oz. aluminium sulphate.
1 lb. 1½ oz. brilliant green extra.

(Pattern No. 74.)

Pulp mixture as for No. 31.

4 oz. 3 dr. naphthol yellow S.
2 oz. 13 dr. auramine O.
2 lb. 3 oz. aluminium sulphate.
14 oz. brilliant green extra.

(Pattern No. 75.)

Pulp mixture as for No. 31.

8 oz. naphthol yellow S.
5¼ oz. auramine O.

Method:

1. **Powder dyes**:

   unambiguous fingerprint.

2. **Dyed paper**:

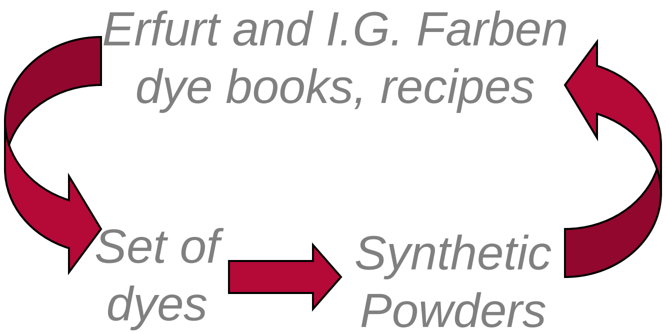
   determine which peaks are detectable

3. **Posadas**:

   Use database and detectable peak information to identify unknown synthetic organic dyes.

Erfurt and I.G. Farben aniline dye books allowed visual matching of the Posadas with aged dyed paper samples.

Twenty reference dyes:

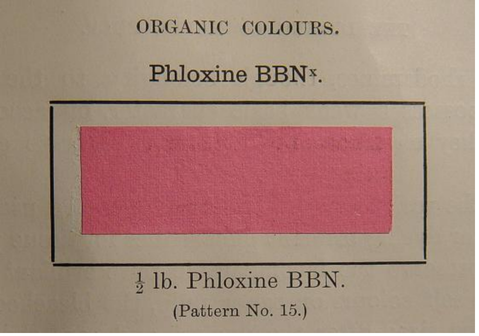


Erfurt and I.G. Farben dye books, recipes

Set of dyes

Synthetic Powders

- Azo (6)
- Triarylmethane (6)
- Xanthene (3)
- Azine (2)
- Diphenylmethane
- Nitro
- Quinoline
- Oxazine
- Thiazine

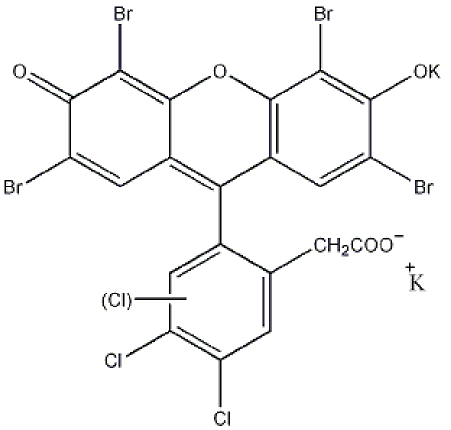


ORGANIC COLOURS.

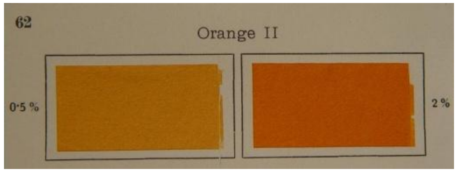
Phloxine BBN×.

½ lb. Phloxine BBN.

(Pattern No. 15.)



Phloxine

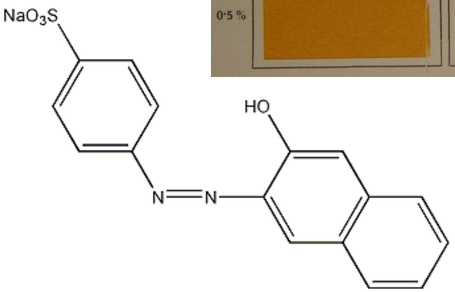


62

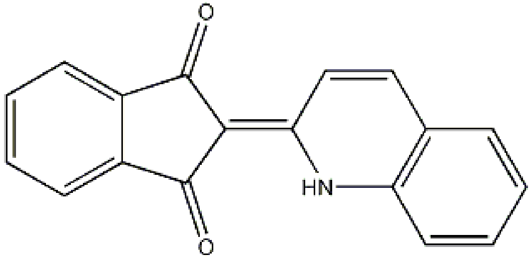
Orange II

0·5 %

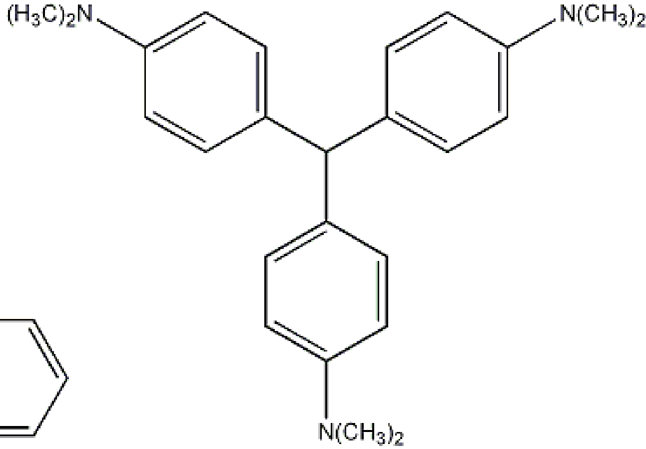
2 %



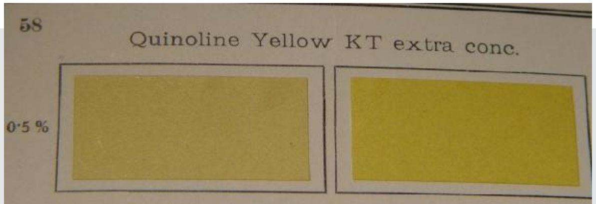
Orange II



Quinoline Yellow



Crystal Violet



58

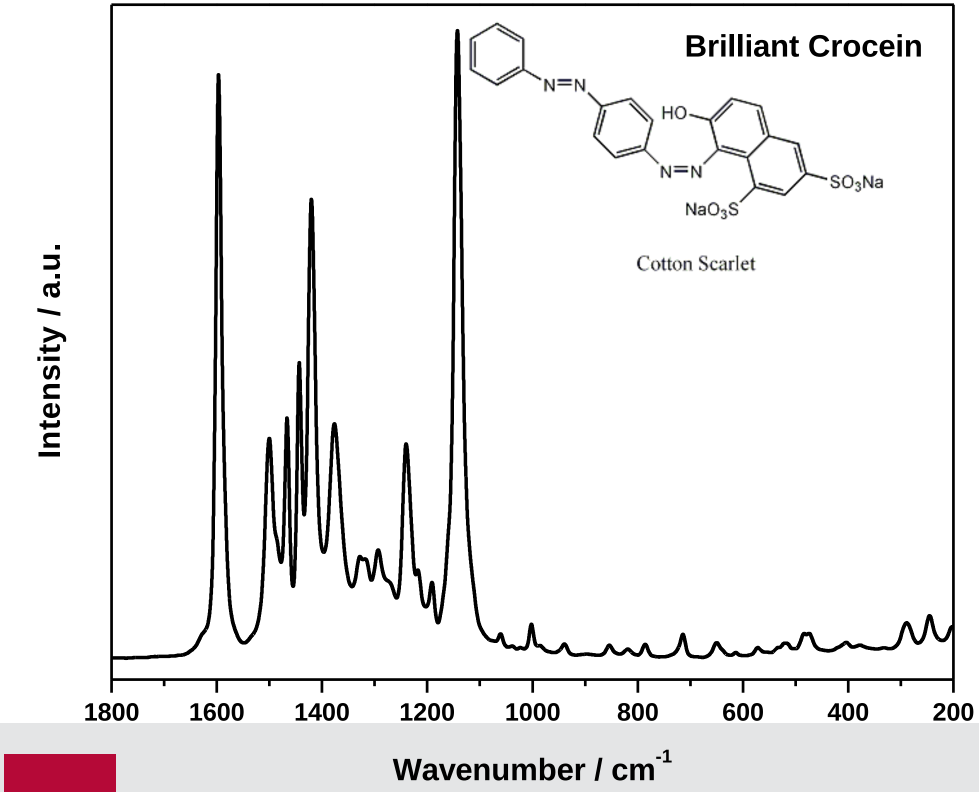
Quinoline Yellow KT extra conc.

0·5 %

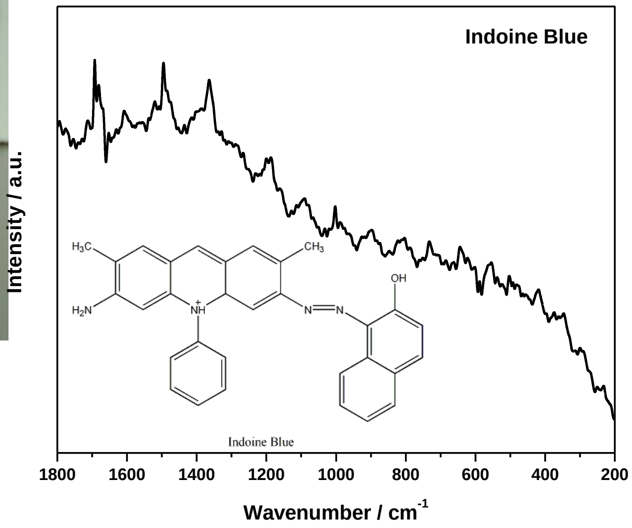
1. Dyes in Powder Form

- Good signal-to-noise
- Good resolution

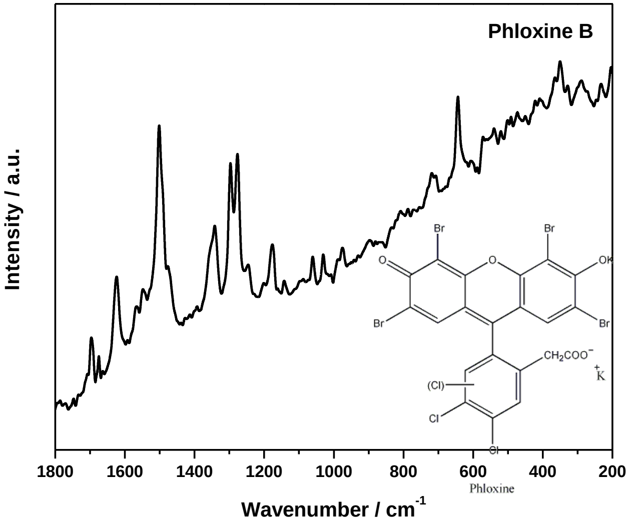
Good spectra (13)



Poor Spectra (3)

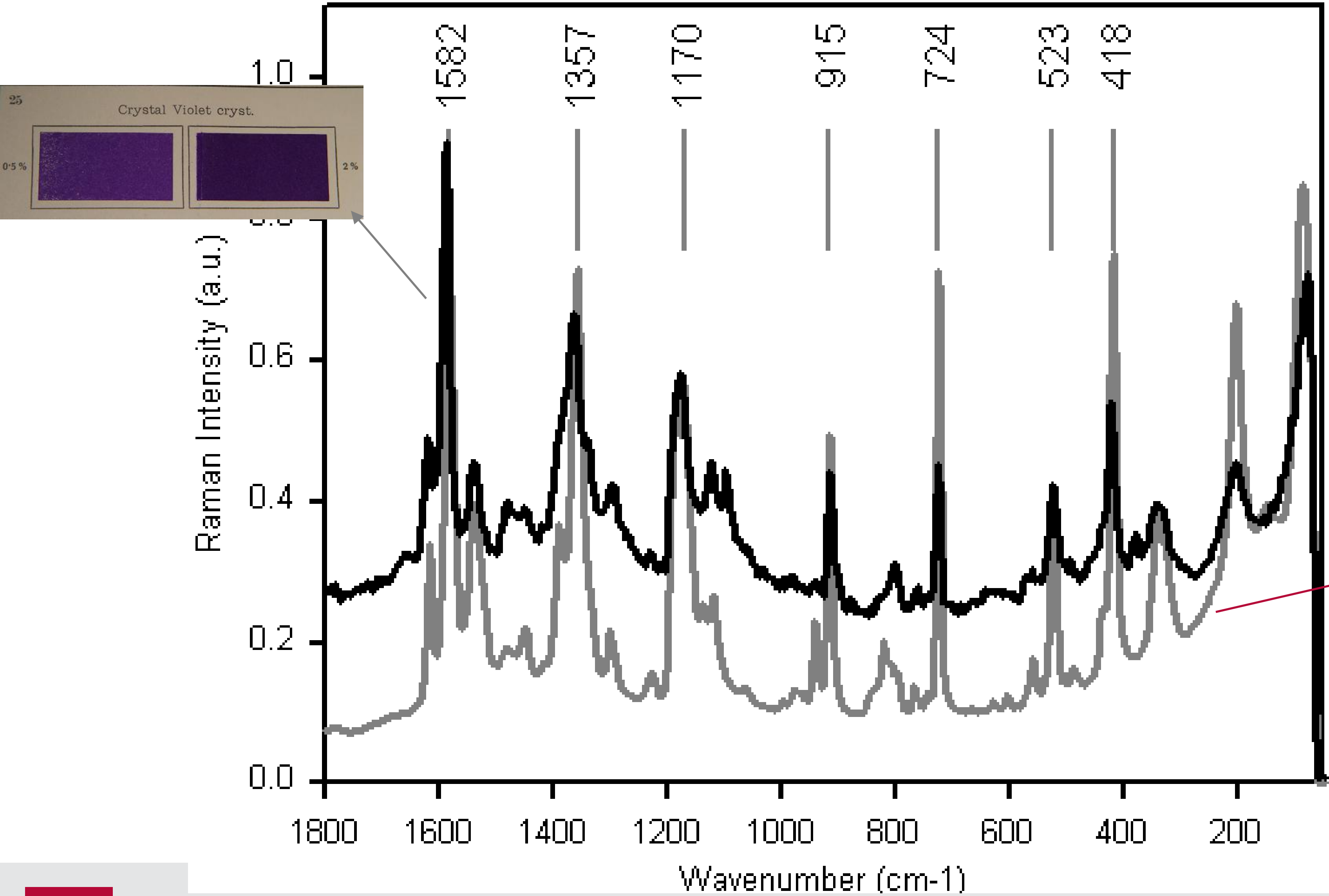


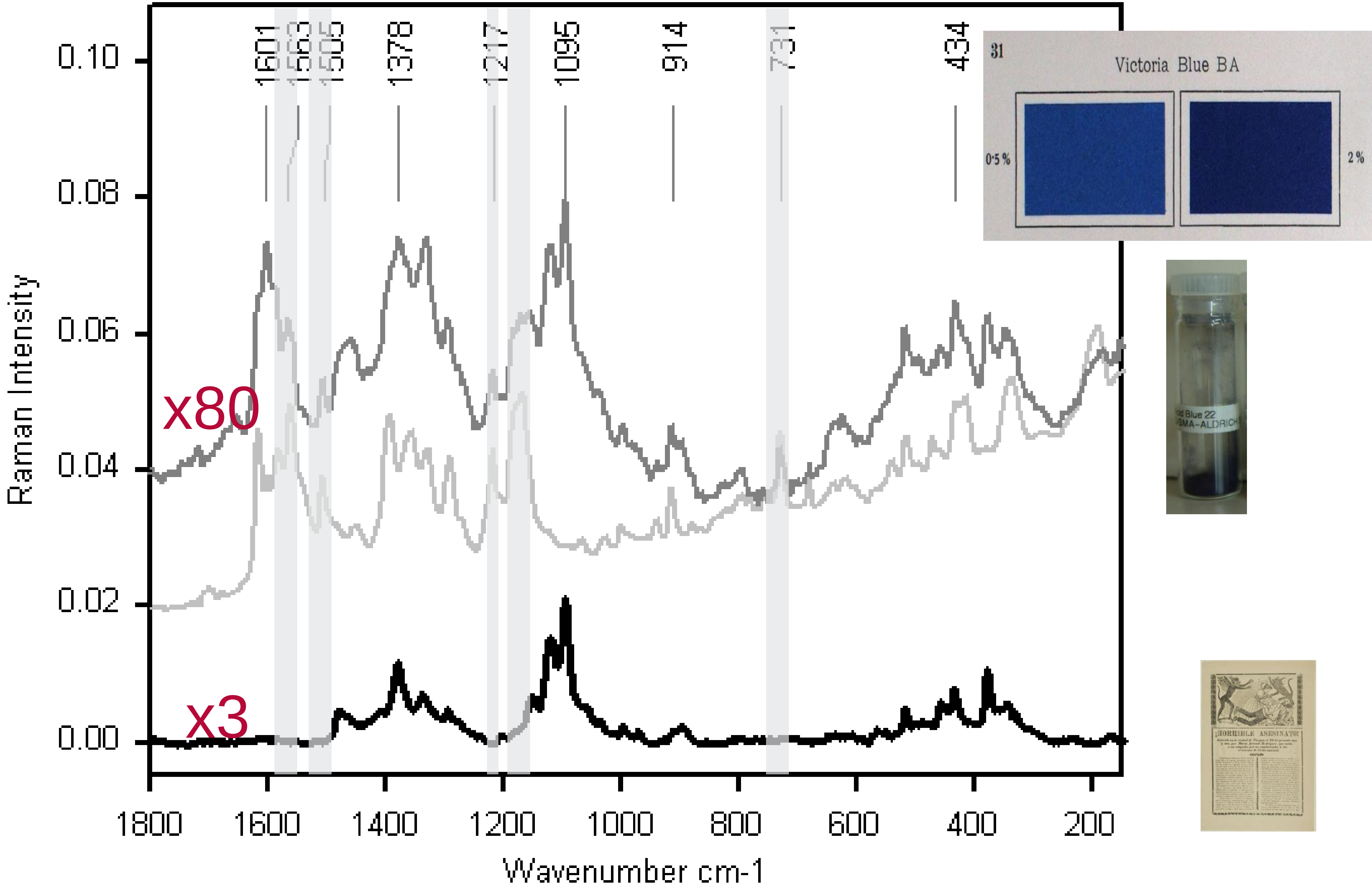
Fair Spectra (4)



2. Dyed paper samples

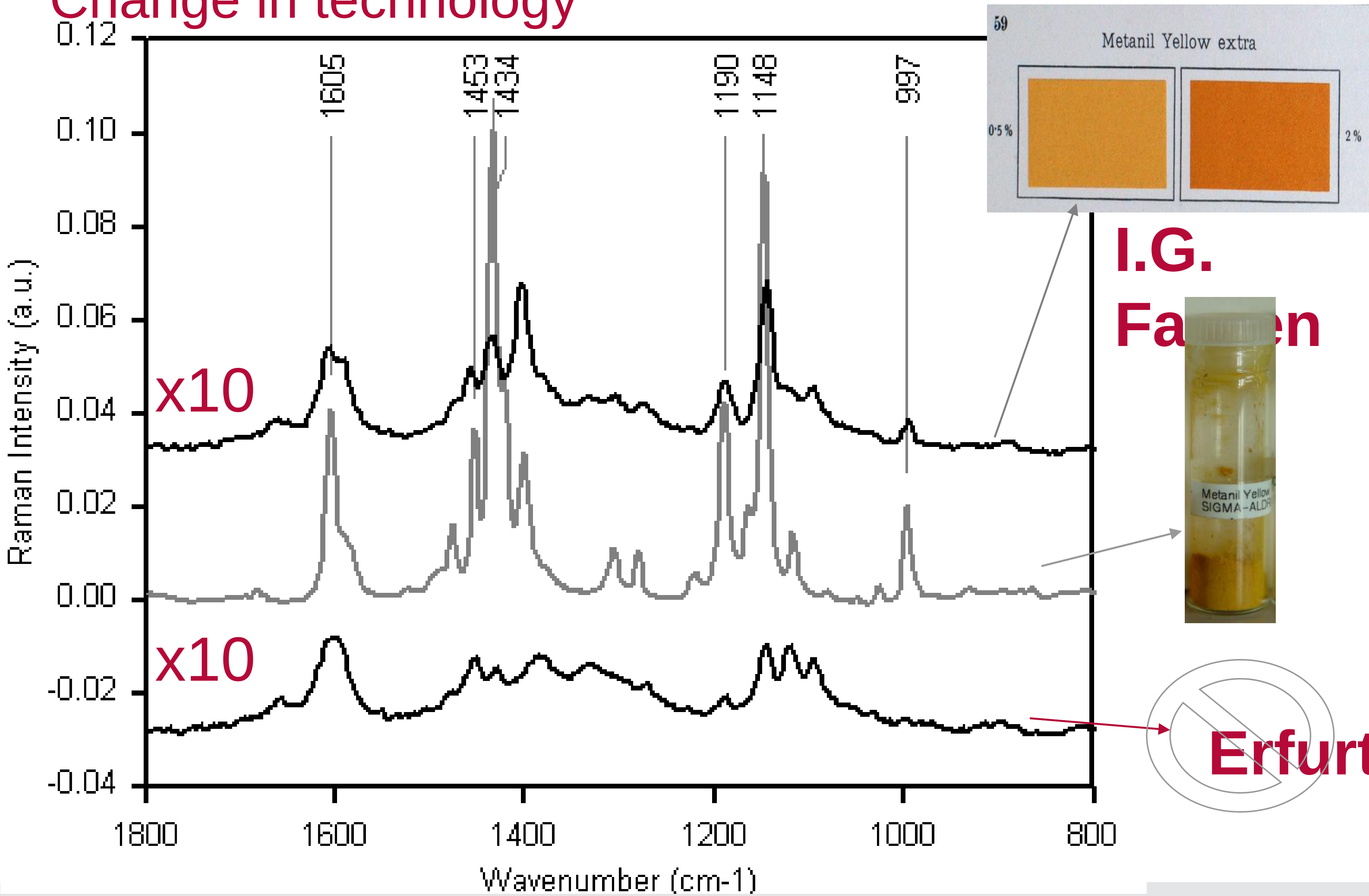
Excellent match




1601
1563
1505
1378
1217
1095
914
731
434
0.10
0.08
0.06
0.04
0.02
0.00
Raman Intensity
x80
x3
1800
1600
1400
1200
1000
800
600
400
200
Wavenumber cm-1
31
Victoria Blue BA
0·5 %
2 %
d Blue 22
GMA-ALDRICH
¡HORRIBLE ASESINATO!

Good match

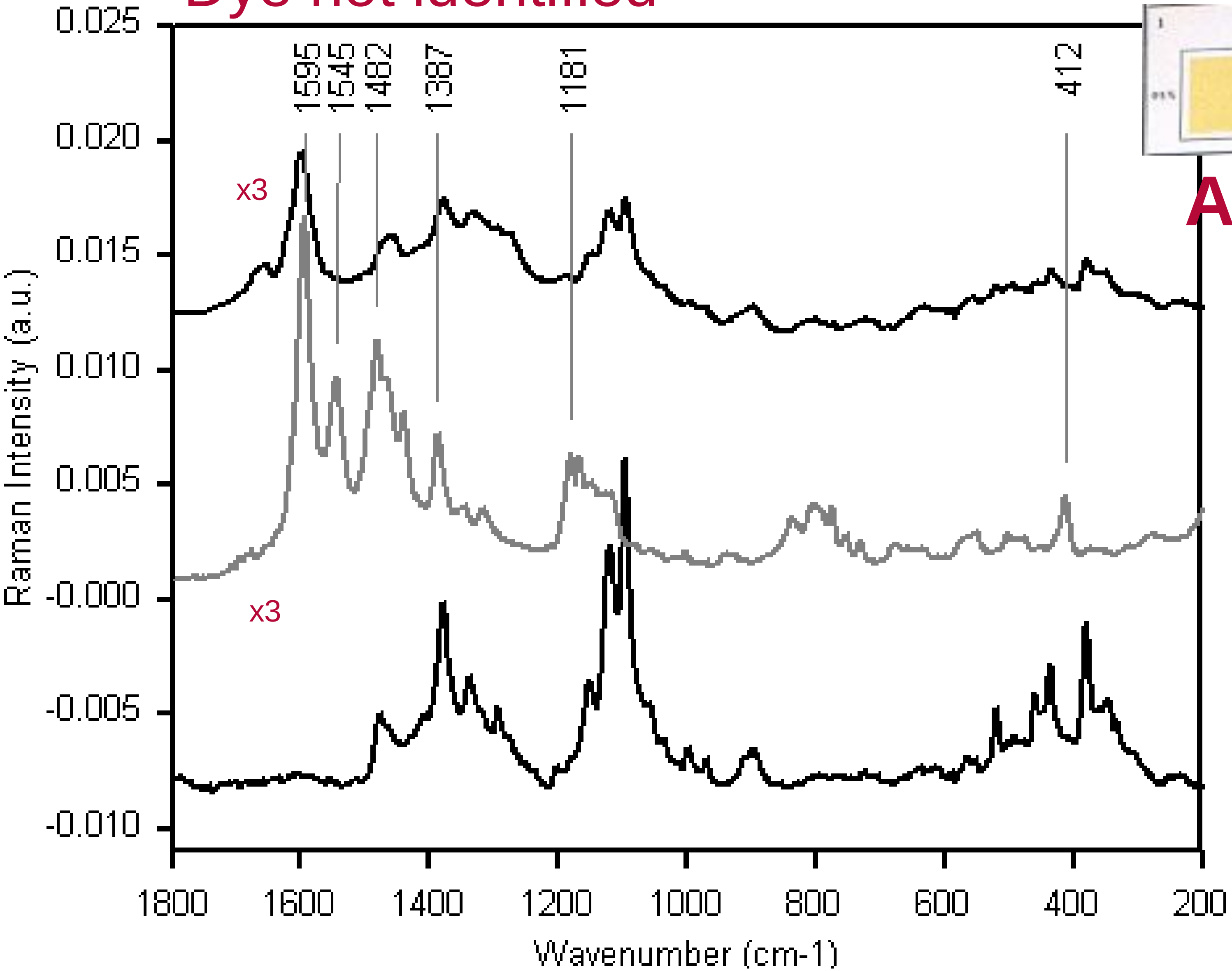
Change in technology

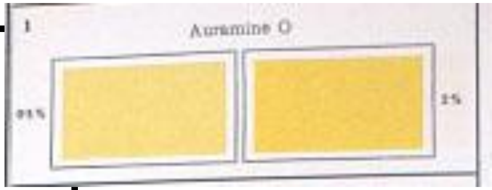


I.G.
Fa en

Erfurt

Dye not identified





Auramine

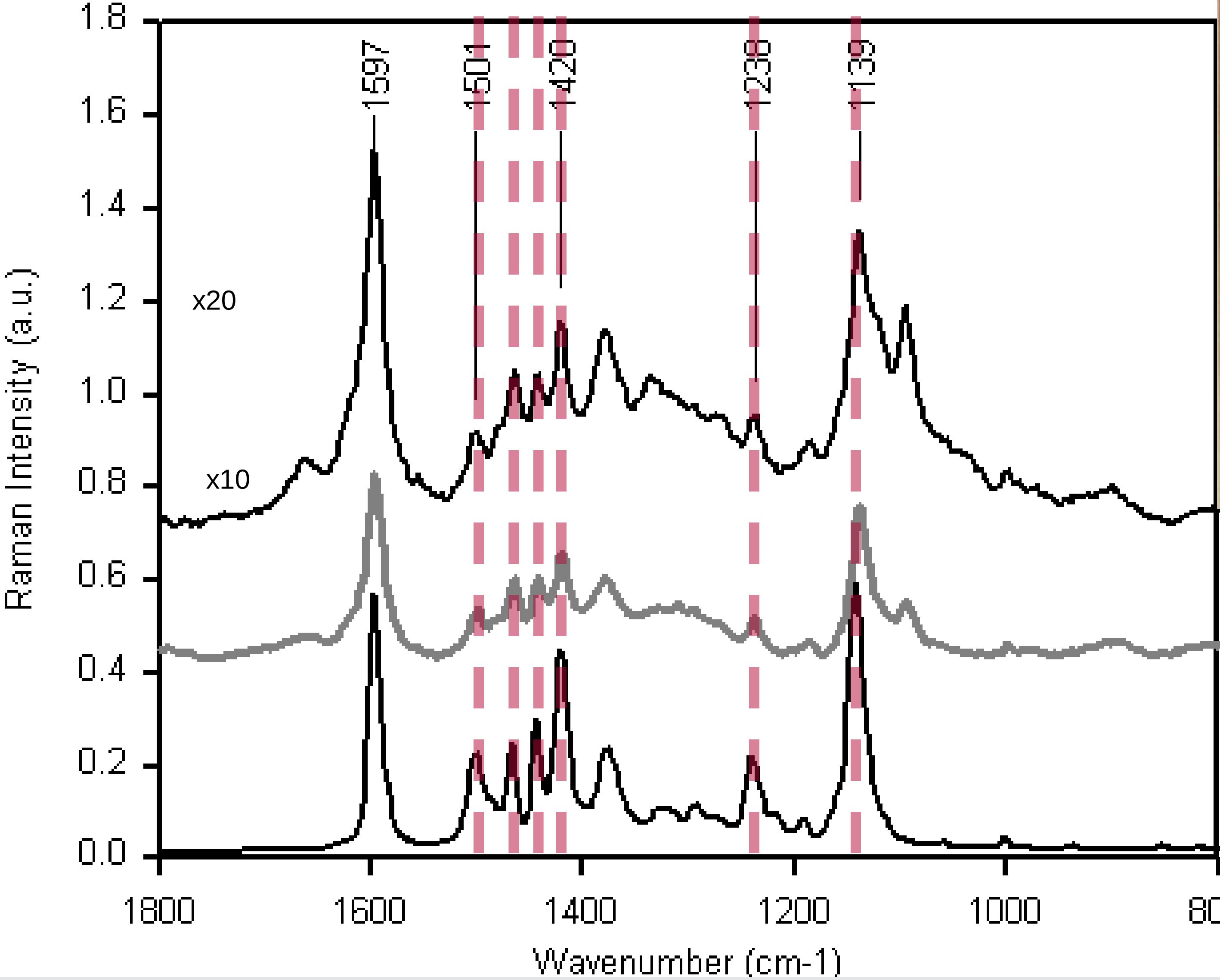
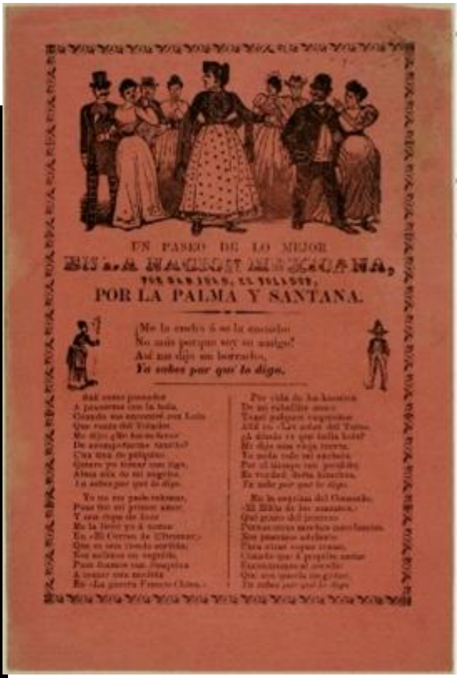
MAMÁ TIERRA CON D. COMETA HALLEY.

El Cometa.—¡Qué estás diciendo insensata?
¡Te atreves á alzar la voz?
¡Pues vas á ver, vive Dios,
Que á mí no me das la lata!

La Tierra.—¡Perdón, don Halley, perdón!
¡Piedad para mis hijitos!
Mira con qué apuración
Corren todos, pobrecitos!

[illegible] á un lado)
[illegible] menudo susto
[illegible] mar á tierra!
[illegible] por puro gusto
[illegible] la guerra
[illegible] del alma

3. Posada prints



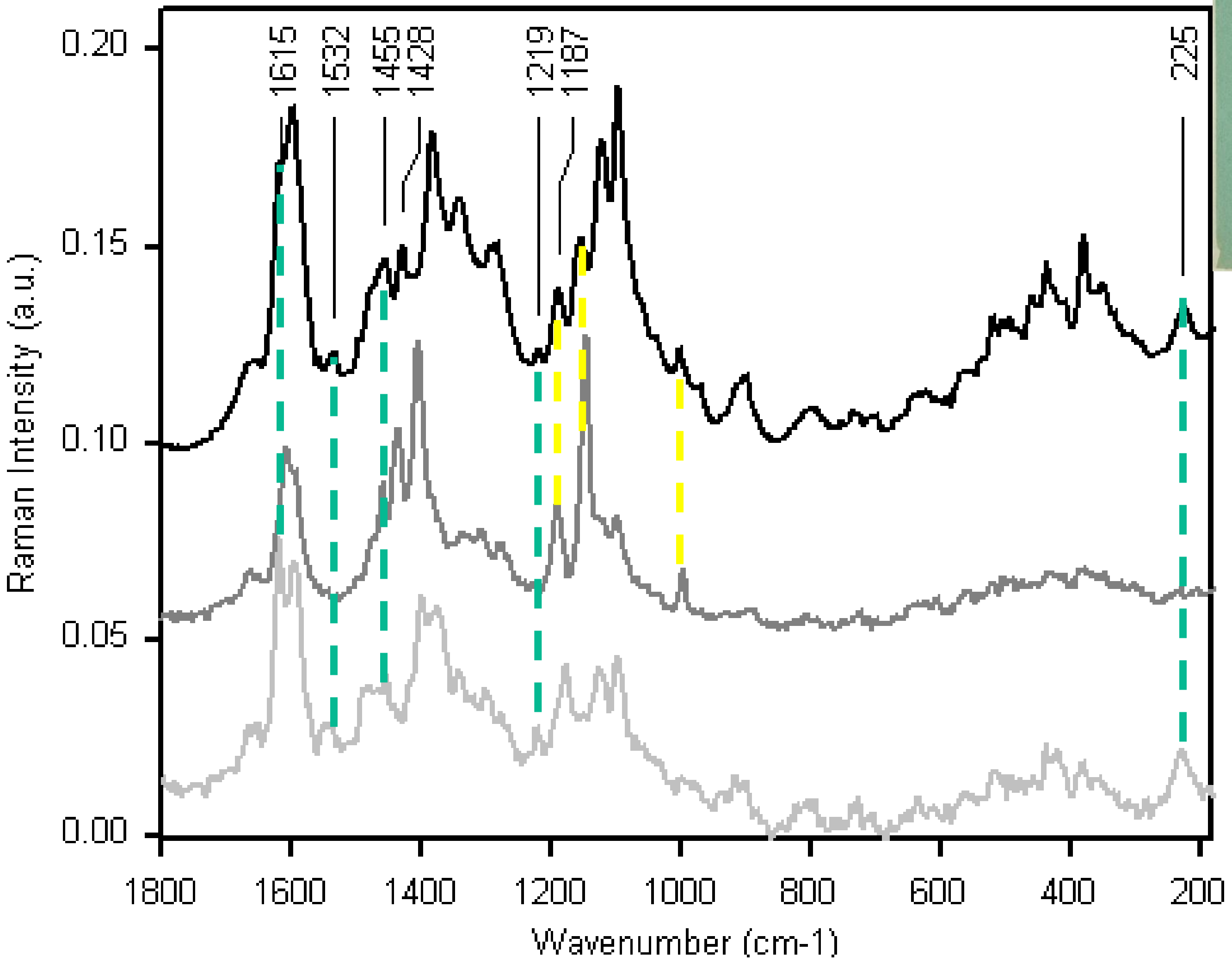
UN PASEO DE LO MEJOR

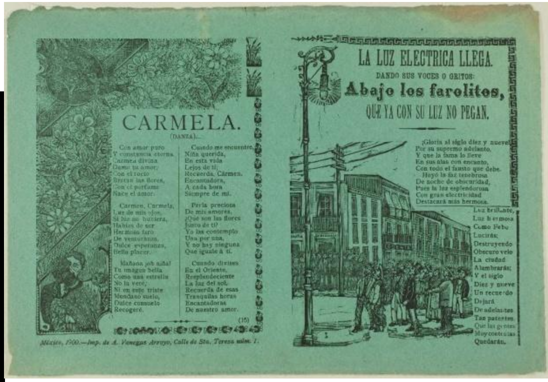
POR LA PALMA Y SANTANA.

Erfurt, Cotton scarlet

Aldrich, Brilliant Crocein

mixtures





CARMELA.

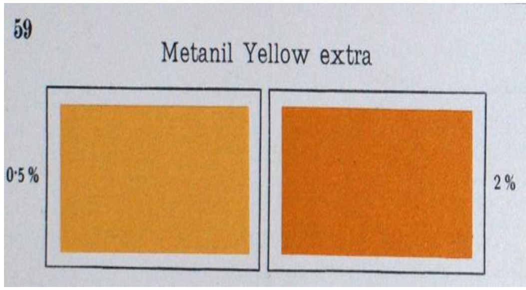
LA LUZ ELECTRICA LLEGA

DANDO SUS VOCES O GRITOS:

Abajo los farolitos,

QUE YA CON SU LUZ NO PEGAN.

1944.103



59

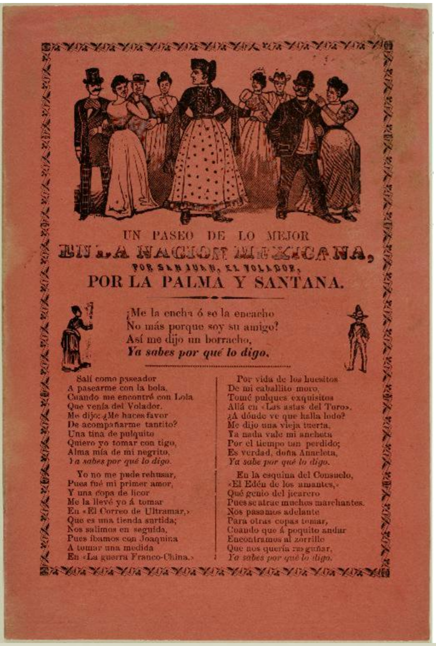
Metanil Yellow extra

0·5 %

2 %

Malachite Green, IG Farben

Conclusions (general):

- FT-Raman is a useful method for analysis of dyed papers
- Early synthetic organic dyes can be detected in dyed paper substrates
- Aniline dyes were successfully detected in Posada's prints, previously thought to be naturally dyed. This has important consequences for conservation (no aqueous treatments, controlled humidity, low light levels) and art historical research

UN PASEO DE LO MEJOR
EN LA NACION MEXICANA,
POR SAN JUAN, EL VOLADOR,
POR LA PALMA Y SANTANA.

¡Me la encha ó se la encacho
No más porque soy su amigo!
Así me dijo un borracho,
Ya sabes por qué lo digo.

Salí como paseador
A pasearme con la bola,
Cuando me encontré con Lola
Que venía del Volador.
Me dijo: ¿Me haces favor
De acompañarme tantito?
Una tina de pulquito
Quiero yo tomar con tigo,
Alma mía de mi negrito,
Ya sabes por qué lo digo.

Yo no me pude rehusar,
Pues fué mi primer amor,
Y una copa de licor
Me la llevé yo á tomar
En «El Correo de Ultramar,»
Que es una tienda surtida;
Nos salimos en seguida,
Pues íbamos con Joaquina
A tomar una medida
En «La guerra Franco-China.»

Por vida de los huesitos
De mi caballito moro,
Tomé pulques exquisitos
Allá en «Las astas del Toro».
¿A dónde ve que halla lodo?
Me dijo una vieja tuerta,
Ya nada vale mi ancheta
Por el tiempo tan perdido;
Es verdad, doña Anacleta,
Ya sabe por qué lo digo.

En la esquina del Consuelo,
«El Edén de los amantes,»
Qué genio del jicarero
Pues se atrae muchos marchantes.
Nos pasamos adelante
Para otras copas tomar,
Cuando que á poquito andar
Encontramos al zorrillo
Que nos quería rasguñar,
Ya sabes por qué lo digo.

EL COMETA DEL CENTENARIO
de la Independencia
1810—MEXICO.—1910

Desde el día 18 de Enero de 1910 observaron en el Telescopio del Observatorio de Tacubaya, un cometa que ha aparecido en las proximidades del sol.

Se observó en Tacubaya dicho cometa como estrella de primera magnitud y la cola era pequeña debido á su cercanía al sol, pues este le opacaba en gran parte. Este cometa se observó desde el 15 del pasado Enero en el Sur de Africa y después en varios puntos de nuestra República, fué visto á pasar de los rayos solares. Se creyó que lentamente iría aumentando en tamaño y le verían en la noche con una magnitud y brillo grandísimo, tal como se veía hace años el cometa de 1882 de inolvidable memoria.

Hasta la tarde del 24 del mes de Enero de 1910 pudo precisarse la marcha del presente cometa, pero de pronto dejó de verse con gran asombro de los habitantes de la tierra.

Este cometa puede titularse de el CENTENARIO. En Coatepec [E. de Veracruz] dicen que fué visto el cabelludo astro á las 11 del día. En California, lo vieron también á medio día y su dirección era al Este del sol y se movía hacia el Suroeste.

Es probable, añadiremos que el cometa dicho al dar la vuelta al sol, haya sufrido grandes trastornos por la acción solar, ó se haya dividido en fragmentos como ha pasado ya con otros; pero nosotros no nos apercibimos de ello, por la gran distancia que hay de la tierra al cometa.

En la actualidad ya se está viendo el gran cometa de Halley; todos los días á la madrugada se levanta la mayor parte de gente alarmada para ver al cometa; saliendo á la calle, balcones ó subiéndose á las azoteas para verlo y prepararse á recibir los temblores y el fin del mundo.

Este Cometa pasará el 18 del presente Mayo

muy próximo á la atmósfera terrestre según cálculos astronómicos. Si pasase penetrando nuestra atmósfera moriríamos, pues los gases del cometa nos ahogarían. Lo único que podrá verse el 18 del citado mes de Mayo será un portentoso torrente de estrellas erráticas ó una aurora polar, siendo digno de admirarse, cualquiera de estos dos fenómenos tan admirables para toda clase de personas en la actualidad.

LA PALOMA AZUL

(DANZA).

Con tus cantos, celestial paloma azul,
Al oír tu acento el ruiseñor se sorprendió,
Alla en el bosque donde tú estabas
Por vez primera te enamoró.
Que te quería te lo juró,
Que te adoraba te aseguró;
Henchido tengo el corazón
Enamorado de tu amor:
Ay! Paloma azul.
Ya nunca vuelvas, pobre avecilla
A dar á nadie tu puro amor,
Que sólo quieren pasar el rato,
Fingiendo siempre loca pasión.
Si alguno pasa y te jura amor,
Corriendo díle, dile que no
Que muerta el alma tienes ya
Desengañada del amor:
Ay! Paloma azul.

Imprenta de Antonio Vanegas Arroyo.—México.

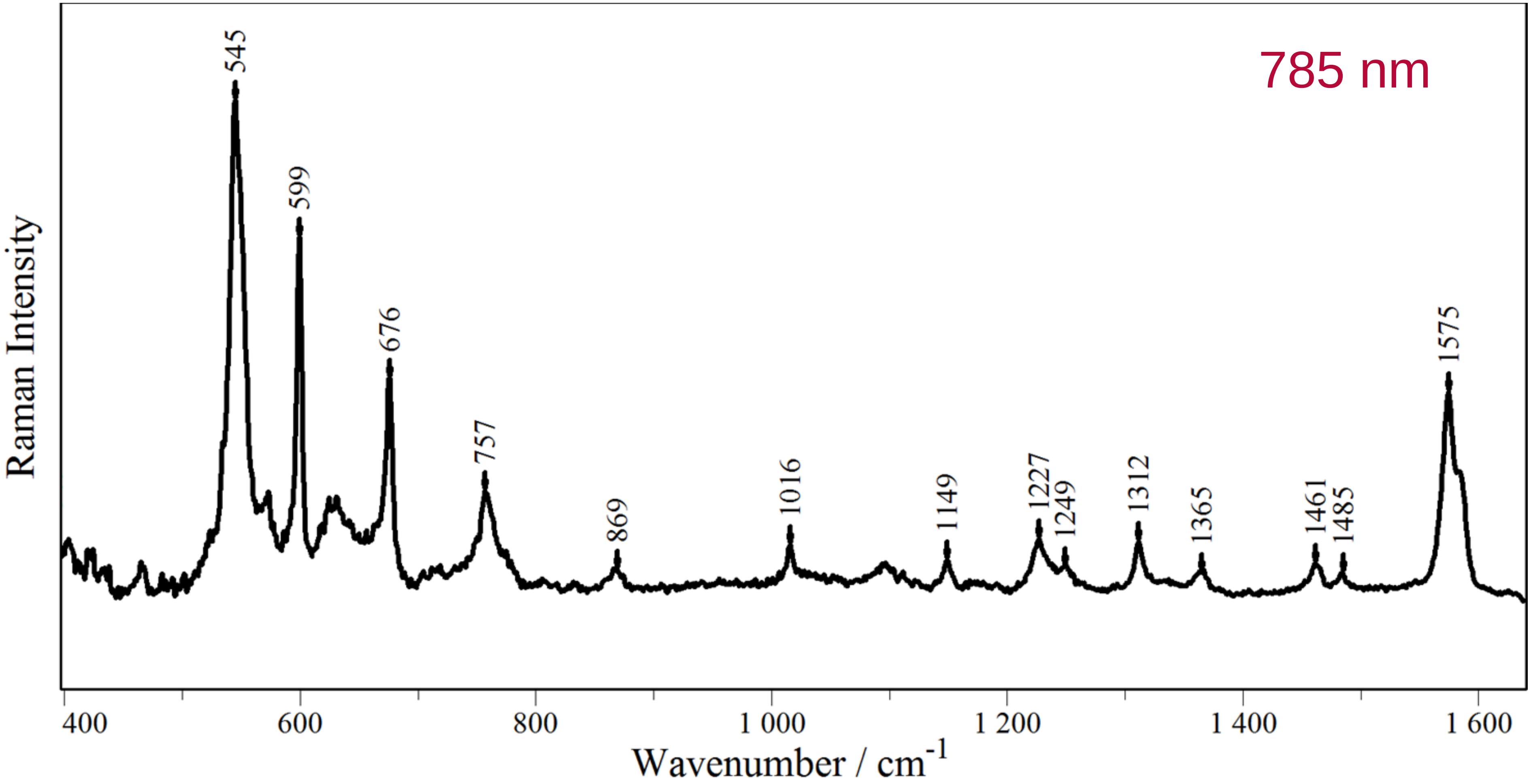
GRAN COMETA Y QUEMAZON,

QUE MUY PRONTO SE VA A VER:
EL MUNDO SE VA A VOLVER
TODITITO CHICHARRON.

¡El mundo se va á acabar! Nos vamos á tostar irremisiblemente! ¡Qué á tostar! Ya quisiéramos! ¡A volvernos ceniza!

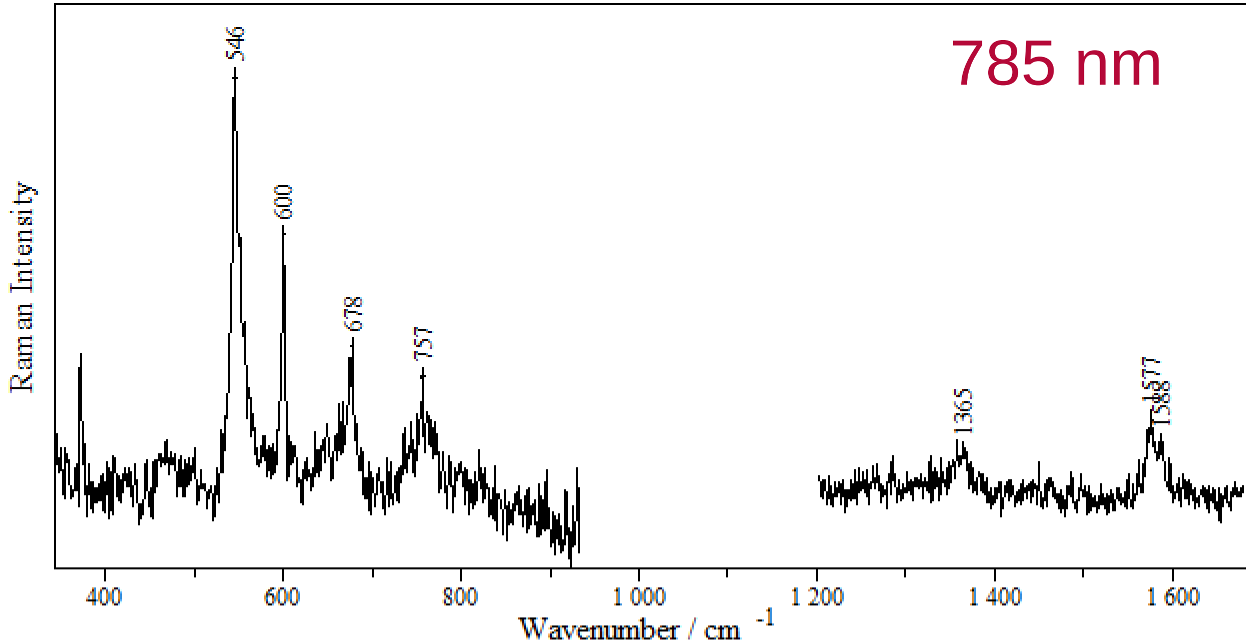
Un gran astrónomo de Europa lo ha predicho últimamente; ya no para Noviembre del año del 1899, sino para el mes de Octubre próximo. Esta catástrofe horrorosísima la va á anunciar el cometa gigantesco que aparecerá en estos dias, este astro malévolo será el que chocará con la tierra, haciendo mil averías, por

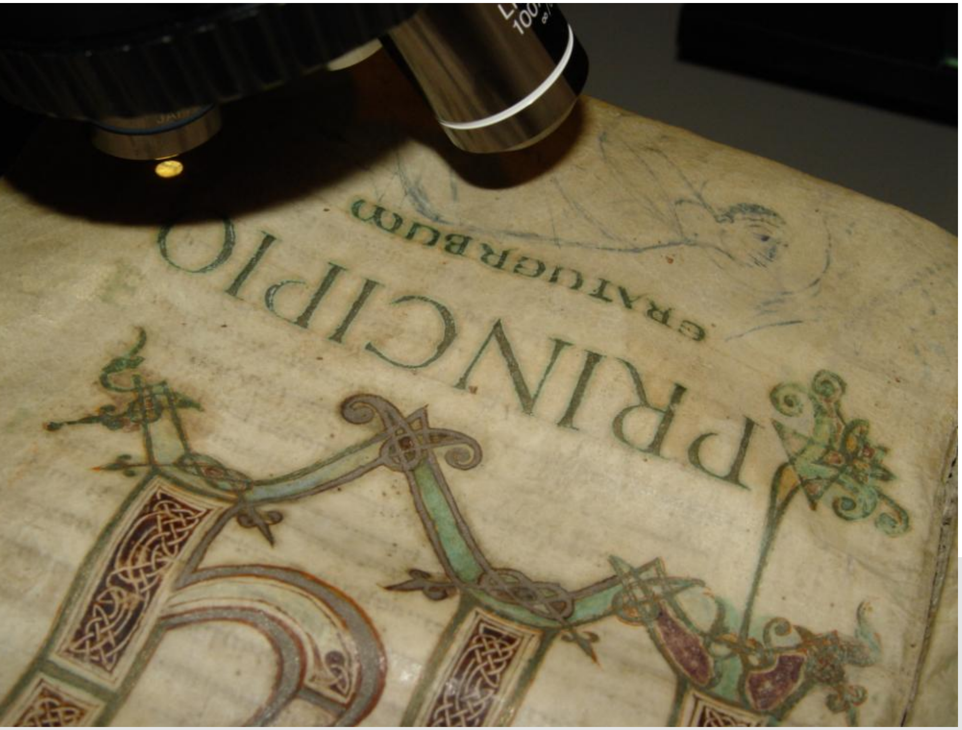
Acquisition Consideration, obj. # 213969. Jean Etienne Liotard, Portrait of a Man Holding a Book



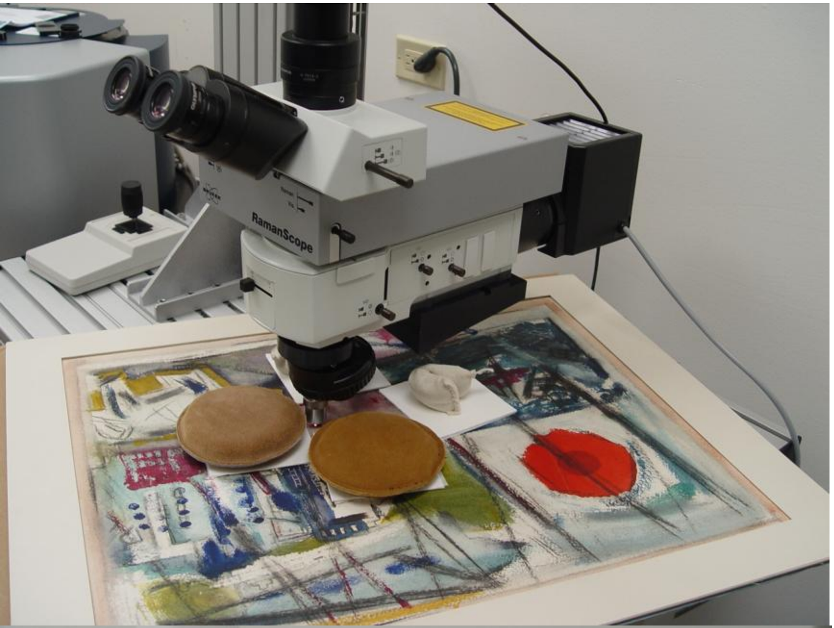
80 secs accu, 2 times

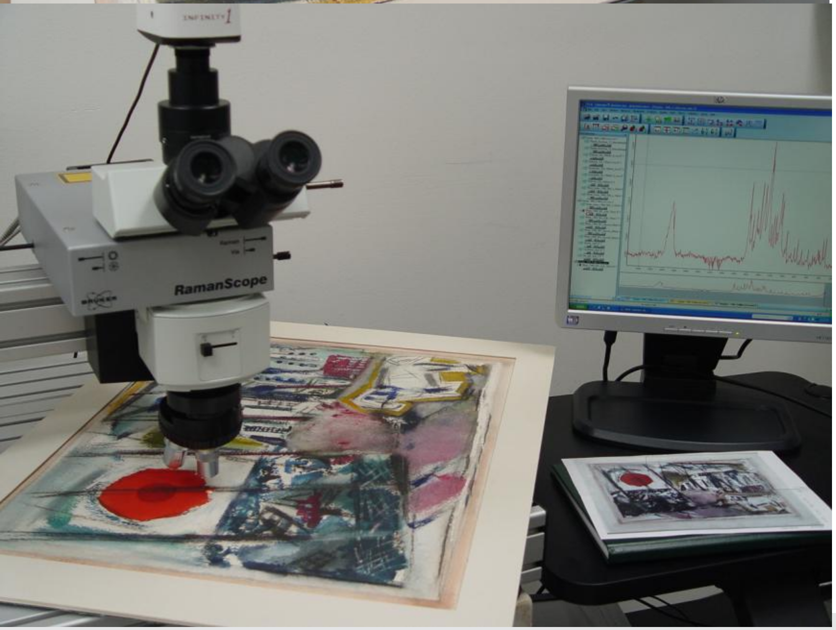
Gospel Book on loan from Hildesheim Cathedral Museum, Hildesheim, Germany 10th century with later additions





Raman spectra recorded on folio 144 of the gospel book, in areas with the blue pigment, indicating Indigotin (λ_0=785 nm; 120 s acquisition, after smoothing and background subtraction)



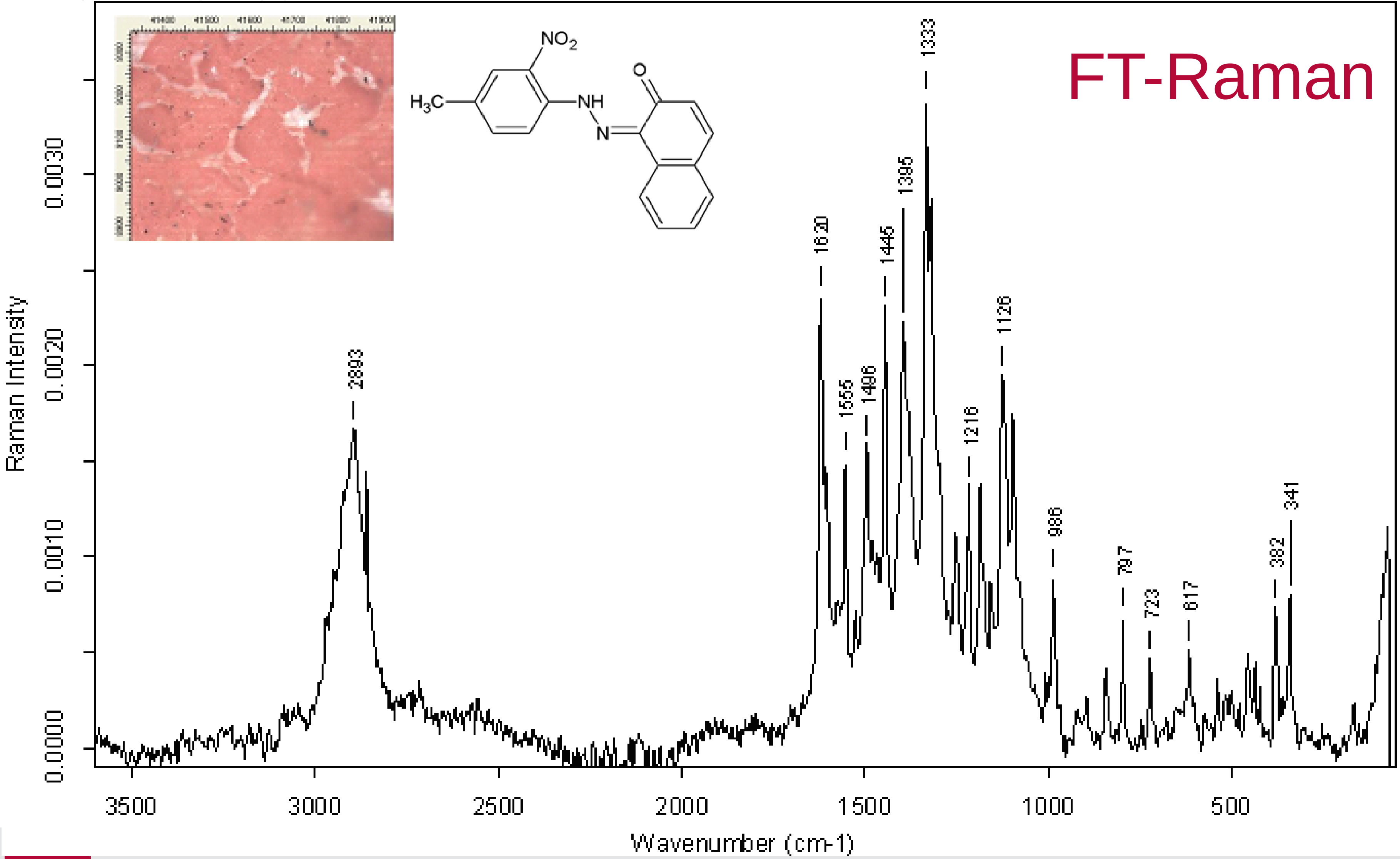


1949.561R, John Marin, The Red Sun – Brooklyn Bridge 1922

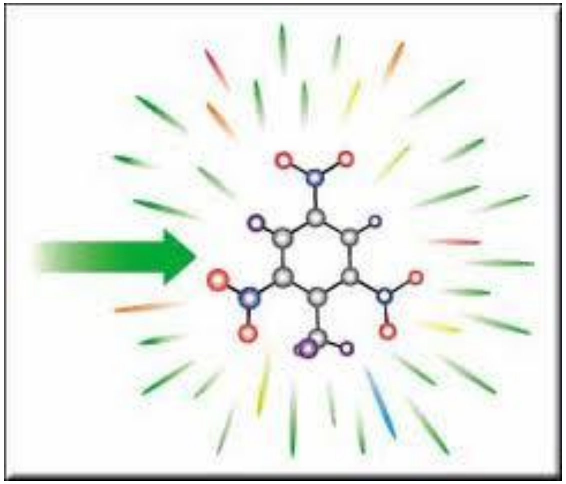
75 mW

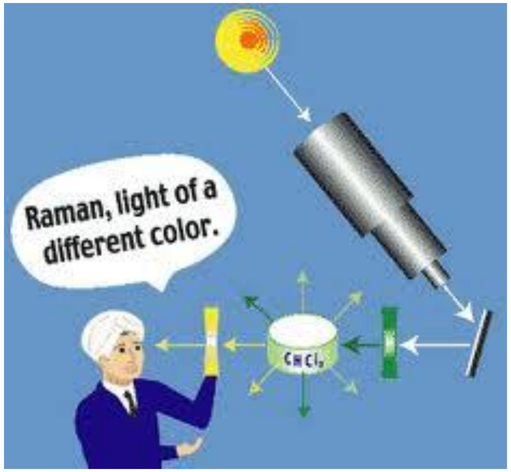
The pigment was first patented in 1905 (see Lomax et al. JAIC 45 (2006)) and it was an extremely widely used red synthetic organic pigment

1621s; 1554m; 1496m; 1445vs; 1395s; 1333vs; 1256; 1217s; 1186s; 1127; 1076; 1057; 985s; 842m; 797s; 723m; 617m; 455m; 383m; 340s; (Scherrer, N.C. et al., 2009)

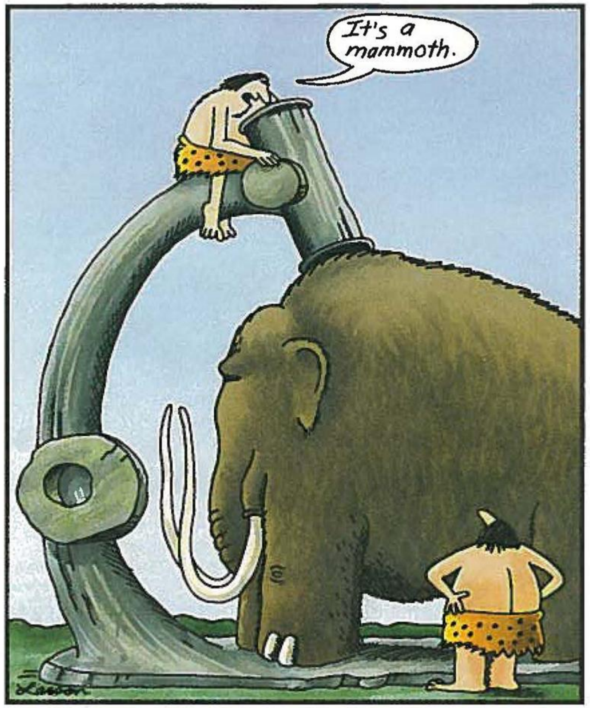


PR3 (Toluidine red) C.I. 12120





- XRF, FORS
- micro-FTIR
- Raman and FT-Raman microscopy
- Scanning Electron Microscopy (SEM-EDX)
- GC/MS, PyGC/MS, DTMS
- HPLC
- XRD
- Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)
- Even Synchrotron techniques…!



Early microscope

Thank you for your kind attention

ART
INSTITVTE
CHICAGO

ACKNOWLEDGEMENTS

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PEOPLE: Rachel Freeman, Meira Chefitz , Katie Mauck, Marcello Picollo, Giovanni Bartolozzi, Eva Grieten, Douglas Severson, F. Zuccari, K. Dahm, H. Stratis; G. Gautier.

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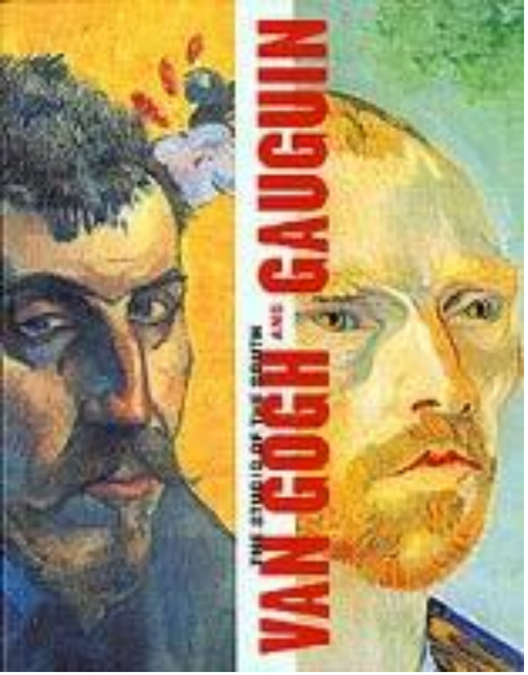
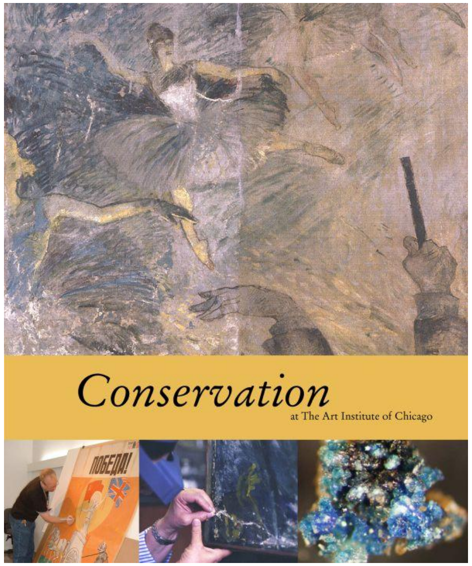
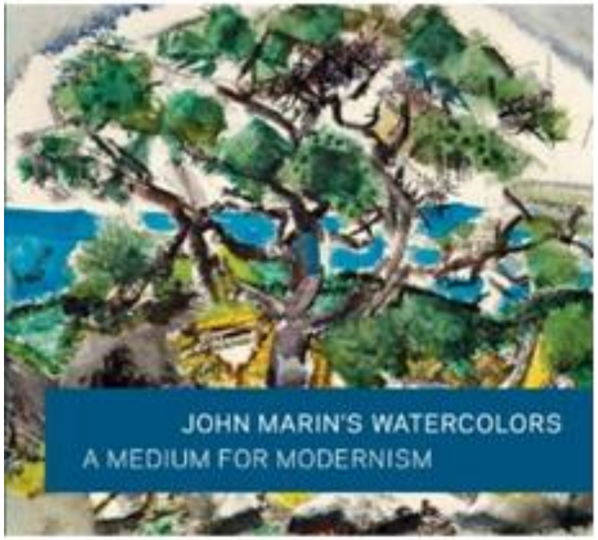
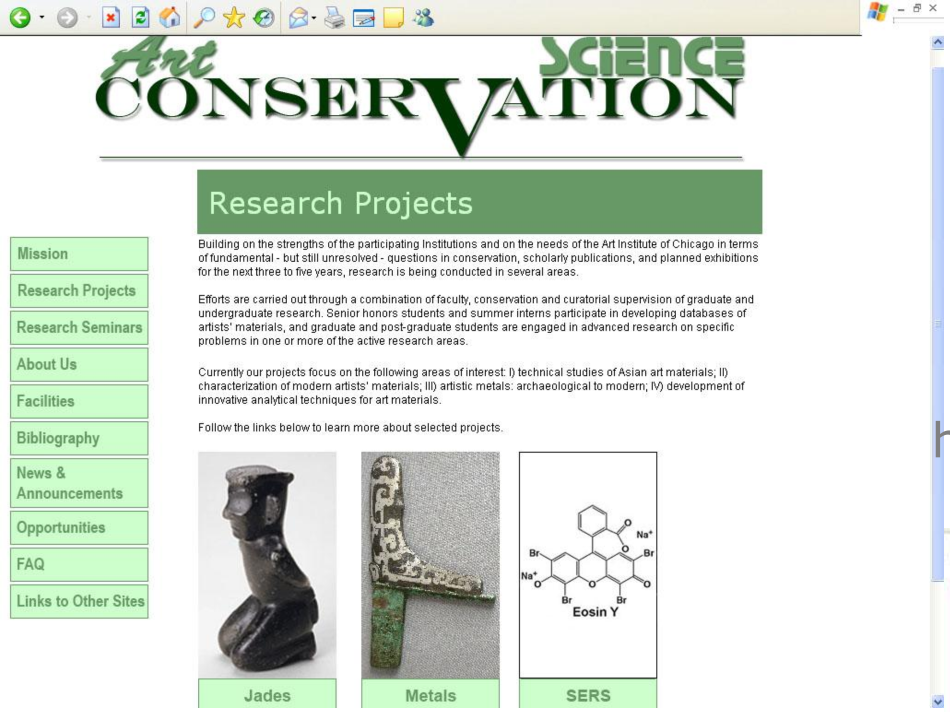






www.artic.edu/aic/conservation/revealingpicasso/index.html



Research Projects

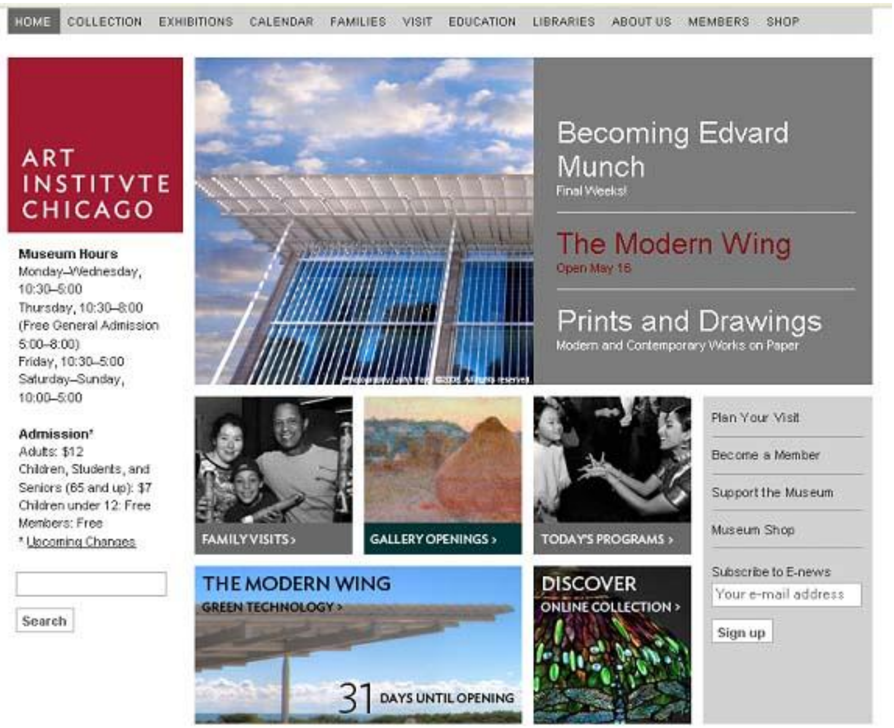
Building on the strengths of the participating Institutions and on the needs of the Art Institute of Chicago in terms of fundamental - but still unresolved - questions in conservation, scholarly publications, and planned exhibitions for the next three to five years, research is being conducted in several areas.

Efforts are carried out through a combination of faculty, conservation and curatorial supervision of graduate and undergraduate research. Senior honors students and summer interns participate in developing databases of artists' materials, and graduate and post-graduate students are engaged in advanced research on specific problems in one or more of the active research areas.

Currently our projects focus on the following areas of interest: I) technical studies of Asian art materials; II) characterization of modern artists' materials; III) artistic metals: archaeological to modern; IV) development of innovative analytical techniques for art materials.

Follow the links below to learn more about selected projects.

http://www.matsci.northwestern.edu/aic



Museum Hours
Monday–Wednesday, 10:30–5:00
Thursday, 10:30–8:00 (Free General Admission 5:00–8:00)
Friday, 10:30–5:00
Saturday–Sunday, 10:00–5:00

Admission*
Adults: $12
Children, Students, and Seniors (65 and up): $7
Children under 12: Free
Members: Free
* Upcoming Changes

www.artic.edu

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Panel discussion & summary

Boris Pretzel

Victoria and Albert Museum, London, UK

FRIDAY, SEPTEMBER 28: DISCUSSION & SUMMARY

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Acknowledgements & invitation to participate

Beth Price, Marcello Picollo

Philadelphia Museum of Art, US; IFAC-CNR, Florence, IT

FRIDAY, SEPTEMBER 28: DISCUSSION & SUMMARY

Infrared & Raman Users Group

Raman Spectroscopy Workshop

Support for the workshop was provided generously by:

NCPTT

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FDM

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Infrared & Raman Users Group

Raman Spectroscopy Workshop

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- Abigail Teller
- Reza Vatankhah
- Renee Ward
- Chris Wasson
- Attendees
- Speakers

Invitation to Participate

For Raman DB:

Beth Price, Project Manager, Philadelphia Museum of Art

Suzanne Lomax, Chair Raman Committee, National Gallery of Art (DC)

For IRUG 11 Conference, Museum of Fine Arts Boston, 2014

Richard Newman & Michelle Derrick, Conference Organizers

www.irug.org

For General Information on IRUG:

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