



**INSTITUTO DE FÍSICA**  
**UNIVERSIDADE DE SÃO PAULO**



AULA 7

MAE

**FÍSICA APLICADA AO ESTUDO DE  
OBJETOS DO PATRIMÔNIO  
CULTURAL: MÉTODOS E TÉCNICAS**

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<https://edisciplinas.usp.br/course/view.php?id=42442>

30 de maio de 2017

DISCIPLINA DE PÓS-GRADUAÇÃO INTERUNIDADES EM MUSEOLOGIA

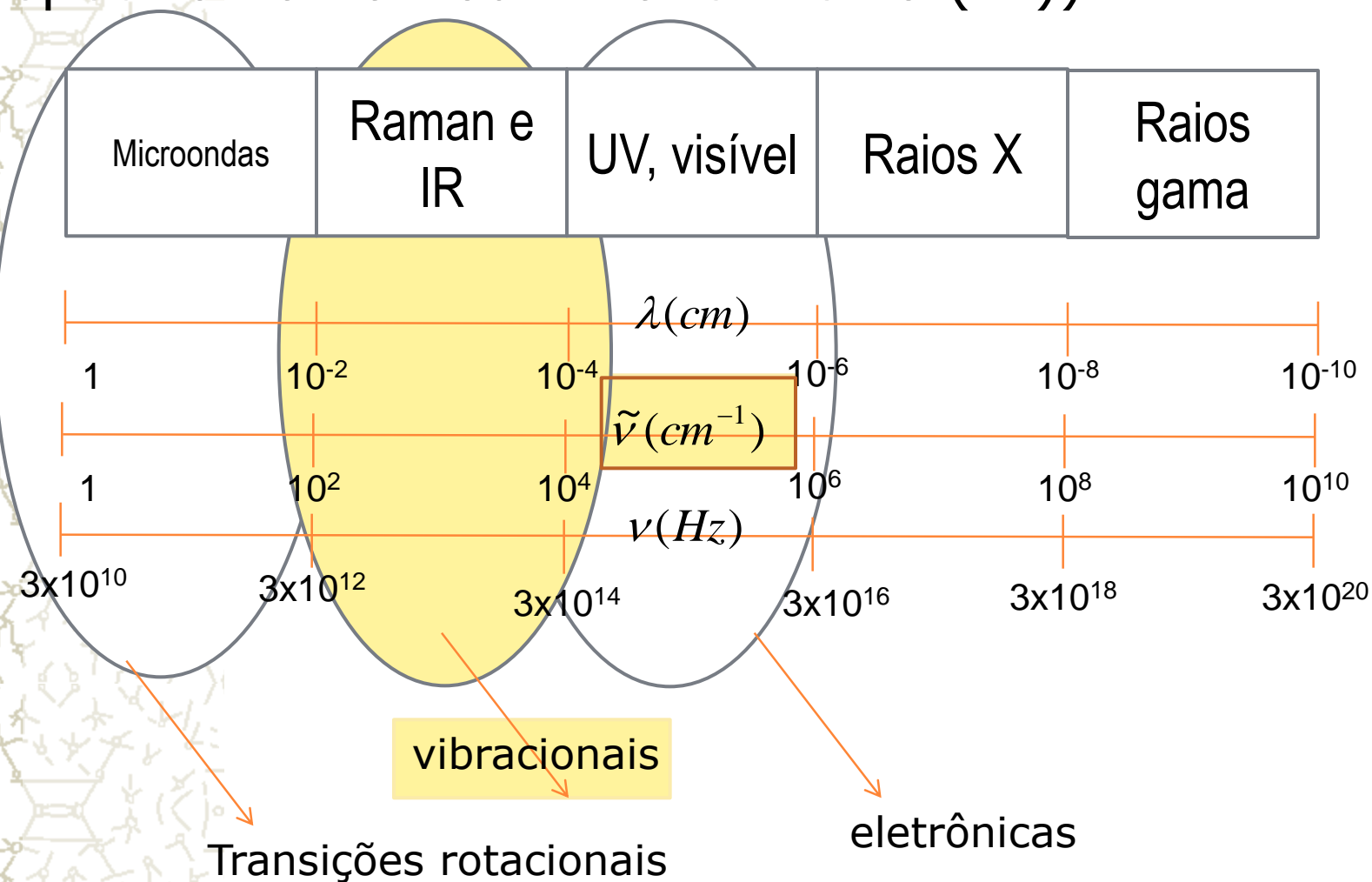
# Programa

- **Capítulo 5 – Análises composicionais e estruturais**
  - Princípios Básicos das técnicas de infravermelho, Raman e Difração
    - Espectrometria Raman
  - Espectrometrias de Infravermelho com Transformada de Fourier
    - Estrutura cristalina e Difração
      - Aplicações
- **Capítulo 6 - Ativação Neutrônica e Análises Isotópicas**
  - Princípios Básicos da técnica de ativação neutrônica
    - Separação isotópica e análises
    - Aplicações nas análises de objetos
- **Capítulo 7: Métodos de Datação**
  - Dendocronologia
  - Datação com radiocarbono
  - Termoluminescência
  - Espectroscopia de Massa com aceleradores
    - Aplicações nas análises de objetos

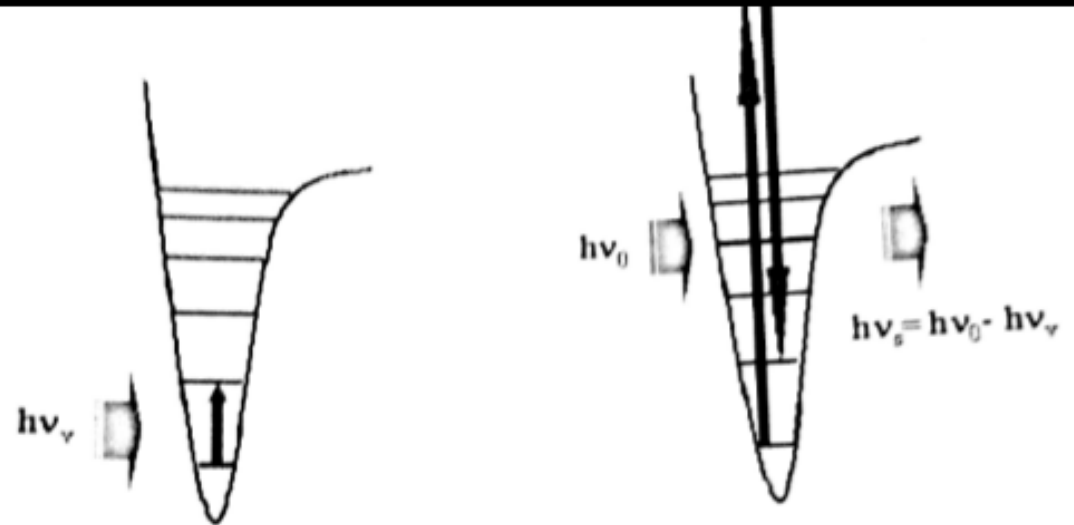
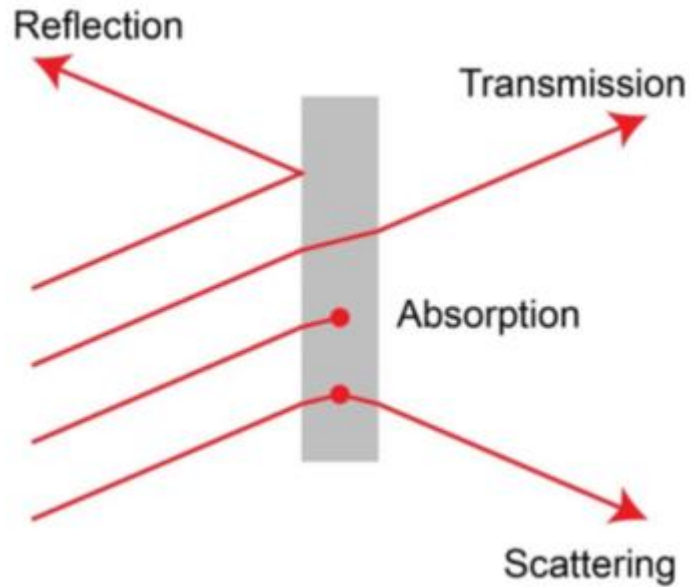
# Espectroscopia Raman e IR



Particularmente estamos interessados nas transições vibracionais (observadas através do espectro Raman ou infravermelho (IR))

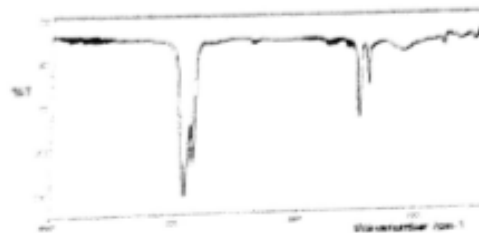


# Espectros Infravermelho e de Raman

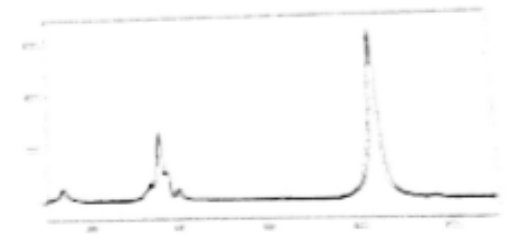


Absorção no Infravermelho

Espalhamento Raman

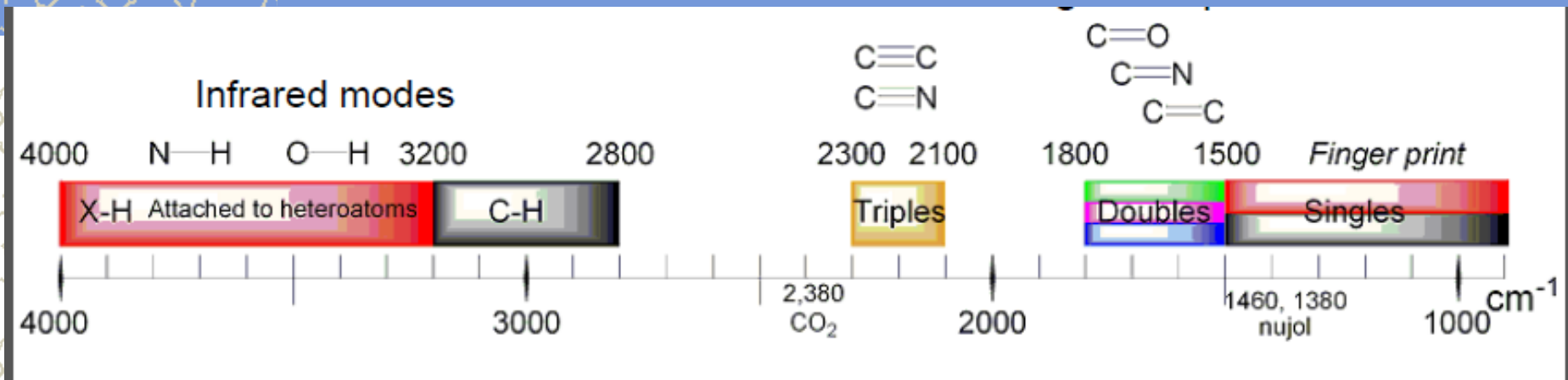


Espectro de absorção no IR

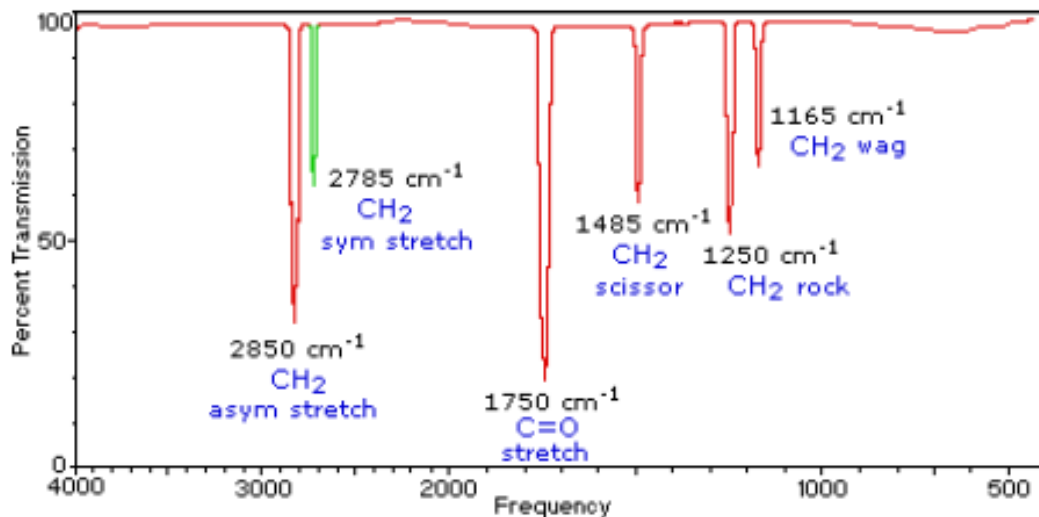


Espectro Raman

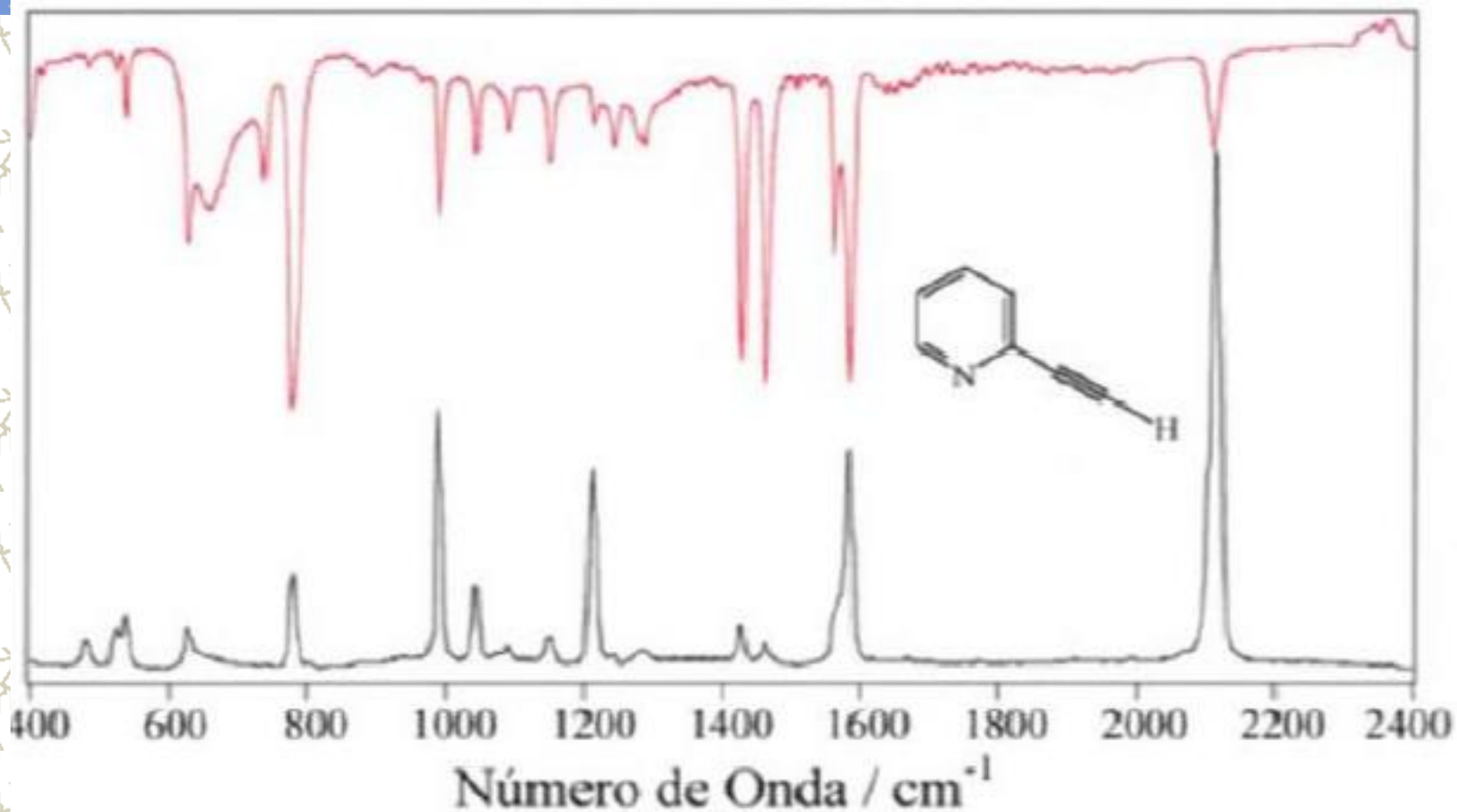
# Espectroscopia infravermelho



Infrared light reflects different modes of vibration & rotation of molecules



# Espectros Infravermelho versus Raman



| Molecule    | Band position<br>$\text{cm}^{-1}$ | Intensity |    |
|-------------|-----------------------------------|-----------|----|
|             |                                   | Raman     | IR |
| Naphthalene | 1630 - 1595                       | w         | m  |
|             | 1580 - 1570                       | vs        | vw |
|             | 1510 - 1500                       | vw        | m  |
|             | 1390 - 1350                       | vs        | ms |
| Anthracene  | 1630 - 1620                       | ms        | ms |
|             | 1560 - 1550                       | vs        | s  |
|             | 1400 - 1390                       | vs        | vw |
| Fenantrene  | 1620 - 1600                       | m         | m  |
|             | 1520 - 1500                       | m         | s  |
|             | 1460 - 1440                       | s         | m  |
|             | 1350 - 1300                       | vs        | w  |

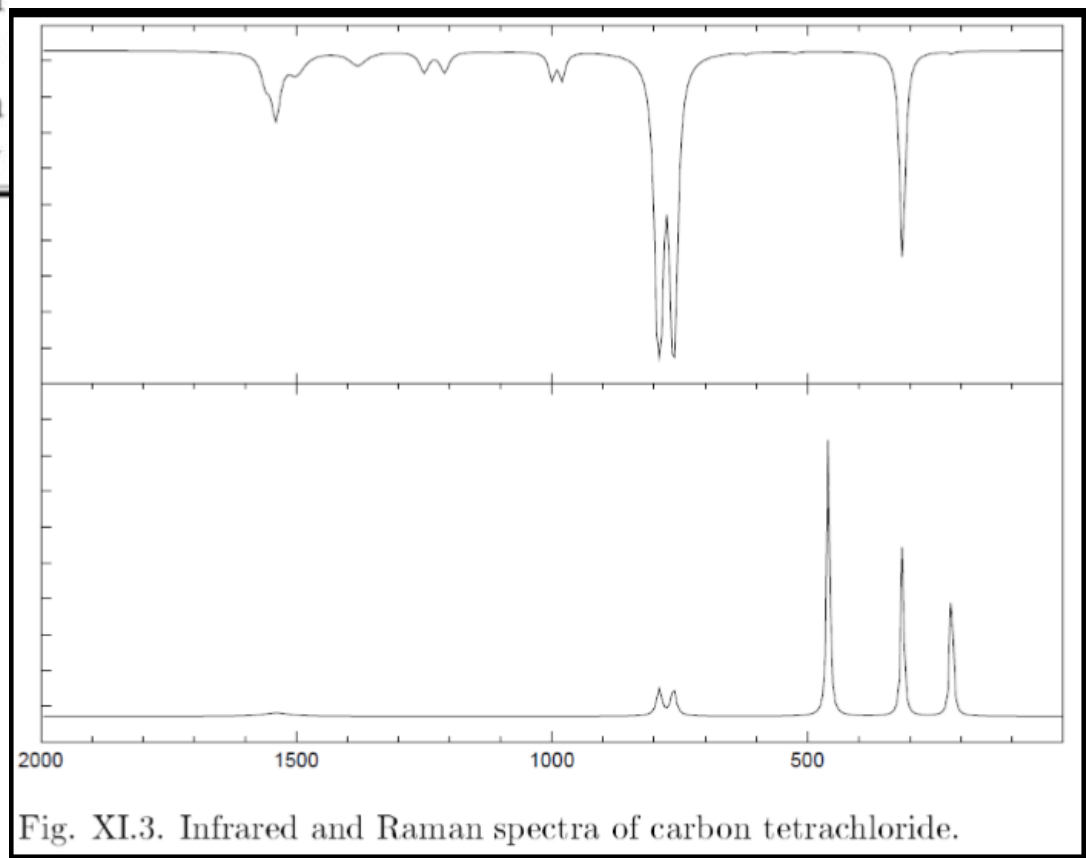


Fig. XI.3. Infrared and Raman spectra of carbon tetrachloride.

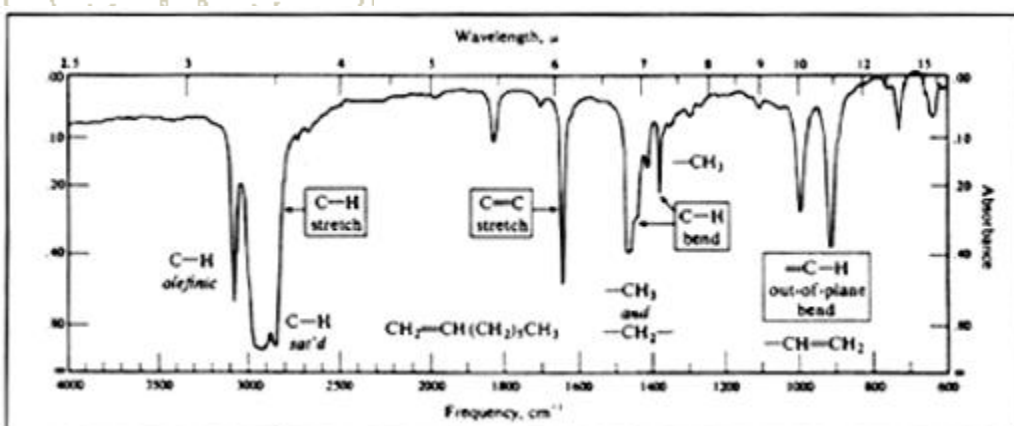


TABLE 3. INFRARED ABSORPTIONS FROM PURE COMPOUNDS

| Wave Number $\text{cm}^{-1}$ | Bonds (s) Responsible  | Name or group or bond                                       | Description and comments**   |
|------------------------------|--|---|--|
| 4000-3120                    | O-H  | alcohol   | strong and broad   |
| 3600-3100                    | $\begin{array}{c} \text{H} \\   \\ \text{-N-} \\   \\ \text{H} \end{array}$      | amine   | medium doublet (1*)<br>singlet (2*)  |
| 3340-3220                    | $\equiv\text{C-H}$   | "sp" C-H bond   | strong and sharp   |
| 3200-3000                    | $\equiv\text{C-H}$   | "sp <sup>3</sup> " C-H bond                                 | variable and sharp,<br>may be doublet  |
| 3000-2830                    | $\text{-C-H}$  | "sp <sup>3</sup> " C-H bond                                 | strong doublet   |
| 2300-2100                    | $\begin{array}{c} \text{C}\equiv\text{C} \\ \text{C}\equiv\text{N} \end{array}$  | acetylene<br>nitrile  | variable, sharp  |
| 1750-1710                    | $\begin{array}{c} \text{-C=O} \\   \\ \text{O} \\   \\ \text{R} \end{array}$     | ester (the C is single-bonded (due to C-O stretch) to -OR') | very strong, sharp   |
| 1725-1680                    | $\text{C=O}$   | ketone  | strong!, sharp/broad   |
| 1700-1630                    | $\begin{array}{c} \text{C=O} \\   \\ \text{N} \end{array}$                       | amide   | strong!, sharp (due to C=O)  |
| 1620-1500                    | $\begin{array}{c} \text{C=C} \\ \text{or} \\ \text{Benzene ring} \end{array}$    | olefin<br>or<br>aromatic                                    | variable, several bands must be confirmed by presence of double-bond C-H at 3040-3000 $\text{cm}^{-1}$<br>several weak overtones |
| 1900-1600                    |  | aromatic  |  |
| 1485-1410                    | $\begin{array}{c} \text{-CH}_2\text{-} \\ \text{or} \\ \text{-CH}_3 \end{array}$ | aliphatic (alkane)  | medium sharp   |

\* The exact location depends on the attached group(s).

\*\* Meaning of Terms

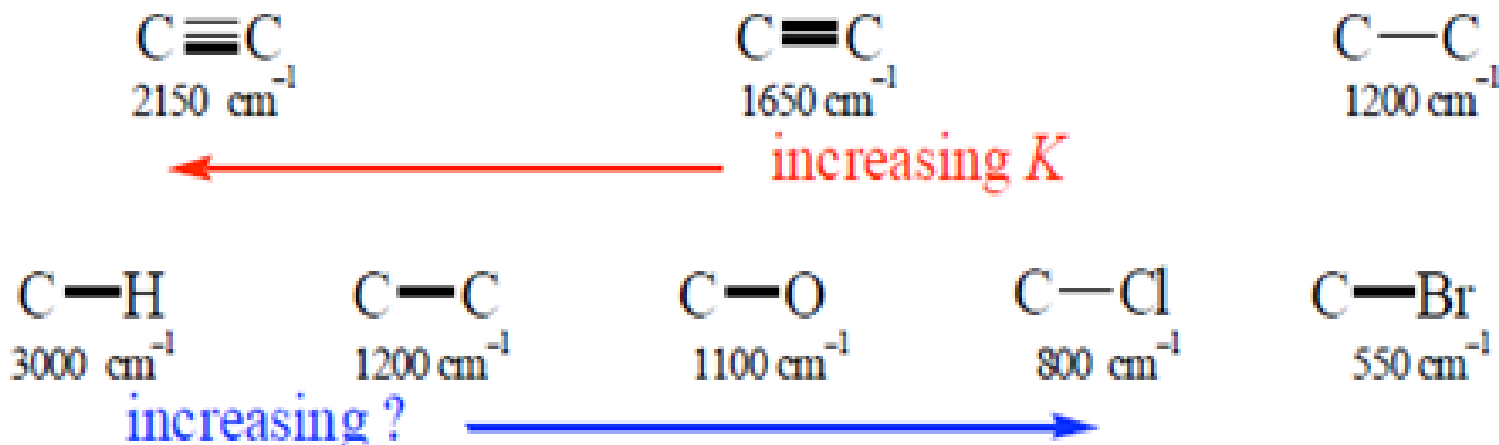
- sharp: an absorption band 10-50  $\text{cm}^{-1}$  wide
- broad: an absorption band 100-300  $\text{cm}^{-1}$  wide
- very broad: an absorption band 400-1000  $\text{cm}^{-1}$  wide
- strong: one of the most prominent bands in the spectrum
- medium: an average band
- weak: a small absorption band; may be obscured easily
- variable: strength and location of these bands depends upon the molecule in question, e.g., the  $\text{-C}\equiv\text{N}$  band can be strong or very weak.



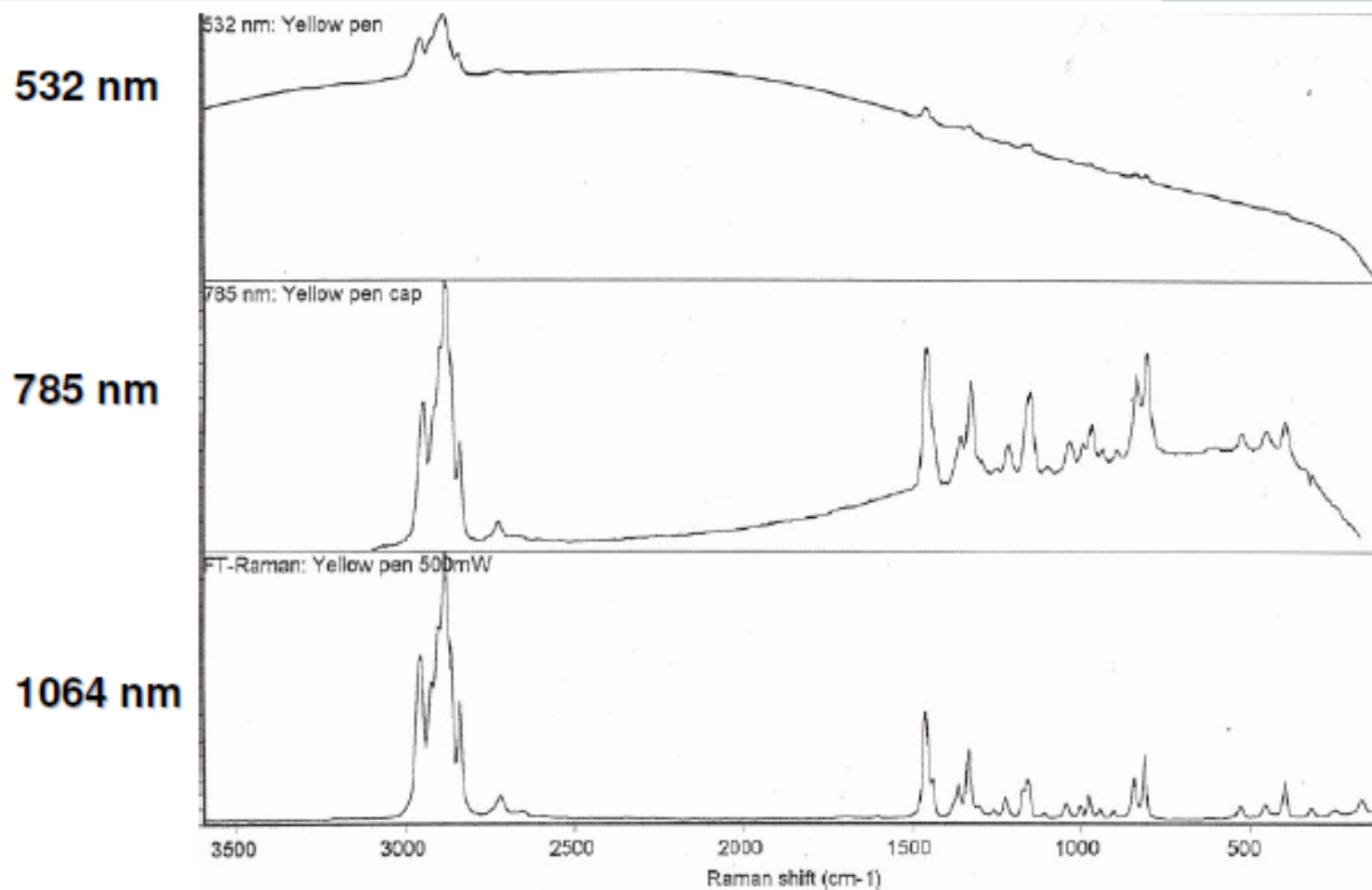
Os picos são usados para identificar os grupos químicos, isto é:  
os tipos de ligação

## EXEMPLOS de frequências características de ligações “stretching” (alongamento)

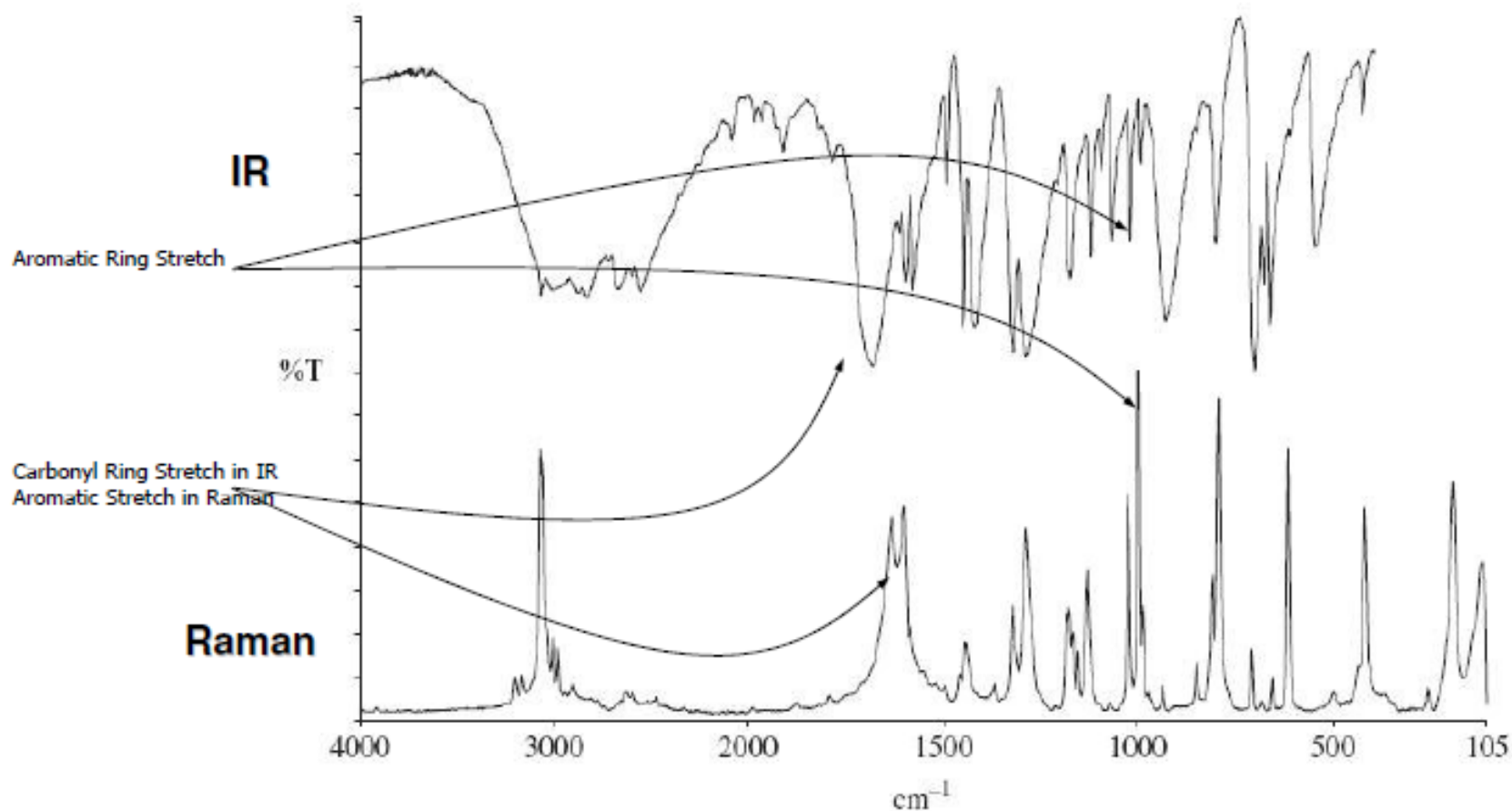
|             |                            |              |                            |
|-------------|----------------------------|--------------|----------------------------|
| O-H         | 3600 $\text{cm}^{-1}$      | C-C          | 1200 $\text{cm}^{-1}$      |
| N-H         | 3400 $\text{cm}^{-1}$      | aromatic C-C | 1450-1600 $\text{cm}^{-1}$ |
| C-H         | 3000 $\text{cm}^{-1}$      | C=C          | 1650 $\text{cm}^{-1}$      |
| C-O/C-N/C-C | 1100-1200 $\text{cm}^{-1}$ | C≡C          | 2200 $\text{cm}^{-1}$      |



# Espectro de uma tampa de caneta



# Espectro de IR e Raman do Ácido Benzóico



# Exemplos espectros Raman com laser de 514.5nm

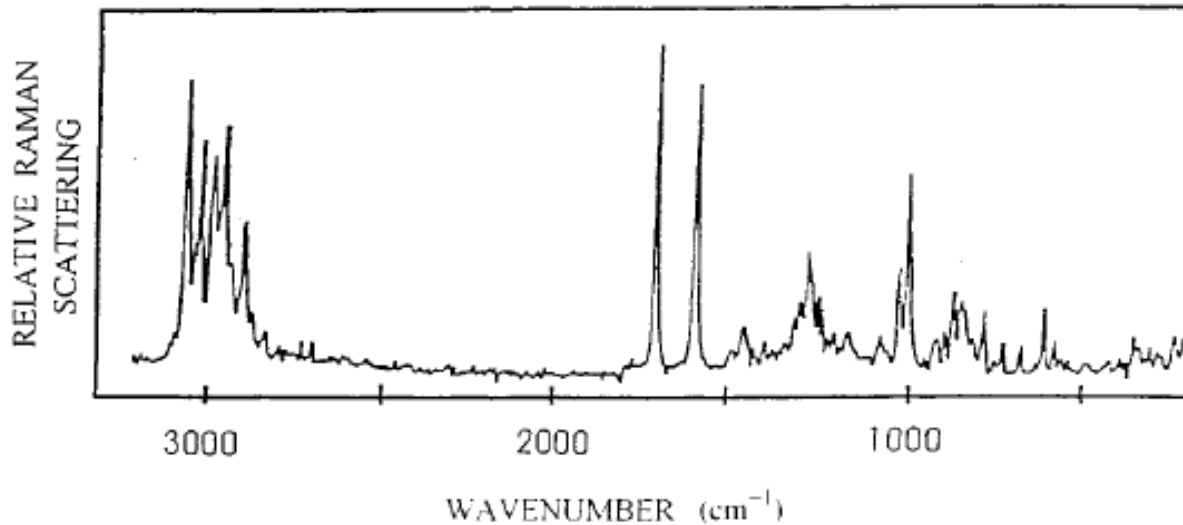


Figure 16 Raman spectrum of cocaine chlorohydrate ( $\lambda_0 = 514.5$  nm; laser power = 0.1 mW).

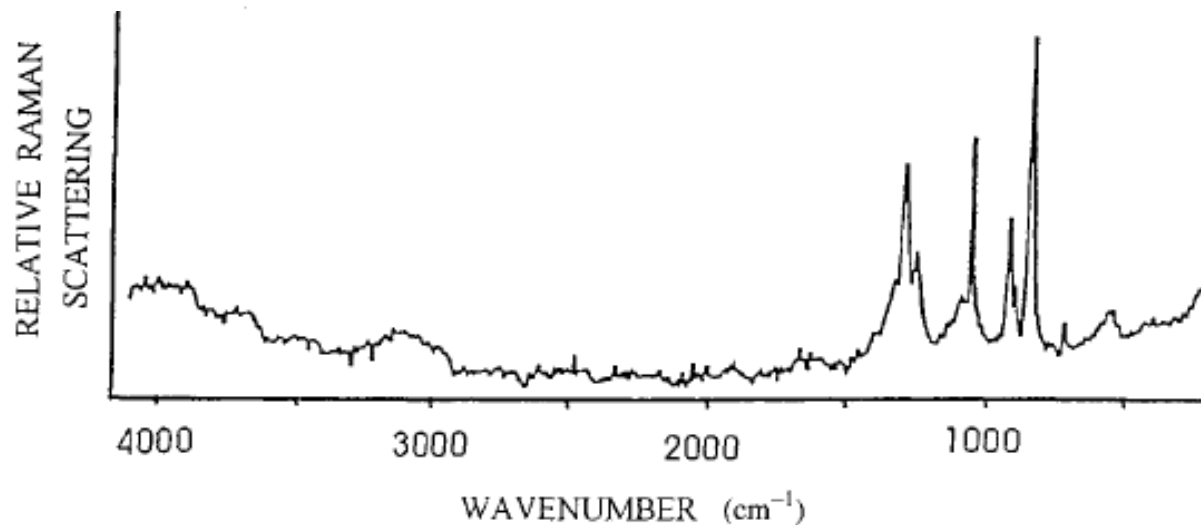
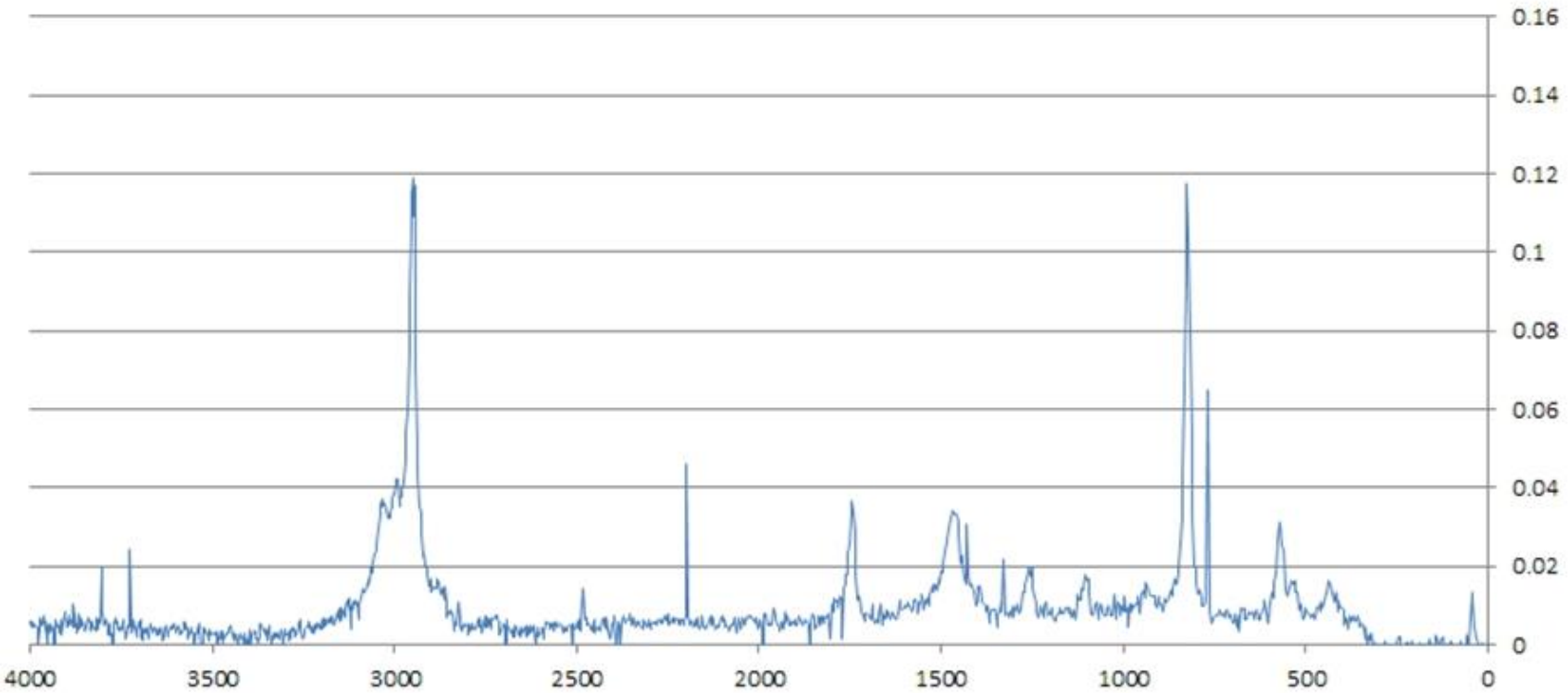
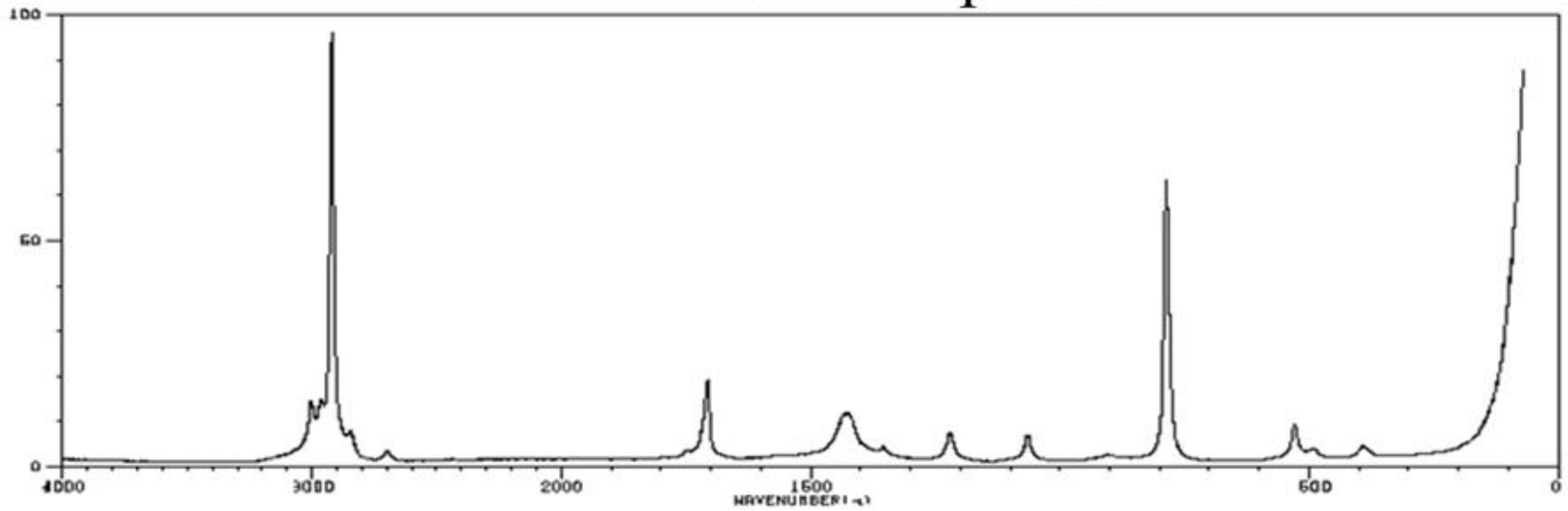


Figure 17 Raman spectrum of nitroglycerine (1% in KBr;  $\lambda_0 = 514.5$  nm; laser power = 500 mW).

# Acetone Raman Spectra



## ***Outras técnicas: RR, SERS and SERRS***

### **RR: Resonance Raman**

Ocorre quando a energia de um fóton do laser coincide com o de uma transição eletrônica de um grupo cromóforo do sistema em estudo.

### **SERS: Surface Enhanced Raman Spectroscopy**

O espectro Raman de uma molécula que é absorvida sobre uma superfície de ouro ou prata pode ter o sinal significativamente aumentado.

### **SERRS: Surface Enhanced Resonance Raman Spectroscopy**

Similar ao SERS, mas usa um laser com energia que coincide com o grupo cromóforo da molécula em estudo.

**SERS / SERRS** podem aumentar o sinal em até bilhões de vezes.



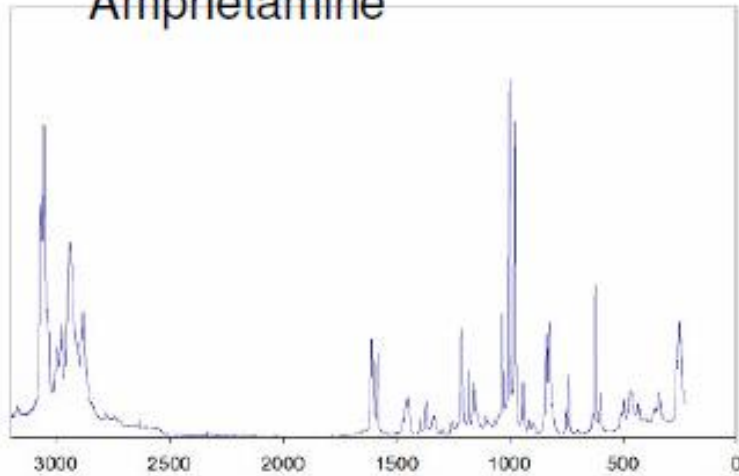
# APLICAÇÕES DA ESPECTROSCOPIA RAMAN

- ✦ Indústria farmacêutica;
- ✦ Carbono e diamante;
- ✦ Material científico;
- ✦ Gemologia, geologia e mineralogia;
- ✦ A ciência forense;
- ✦ Nanotecnologia;
- ✦ Biológicas e biomédicas;
- ✦ **Arte e patrimônio.**

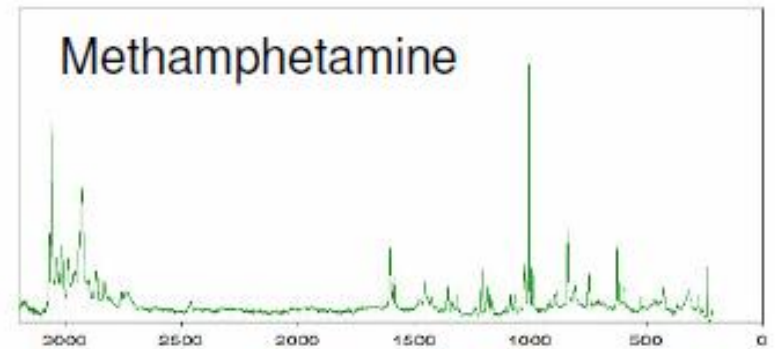
# Aplicações



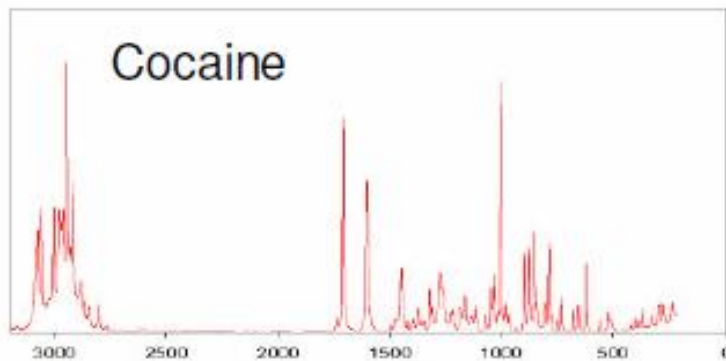
Amphetamine



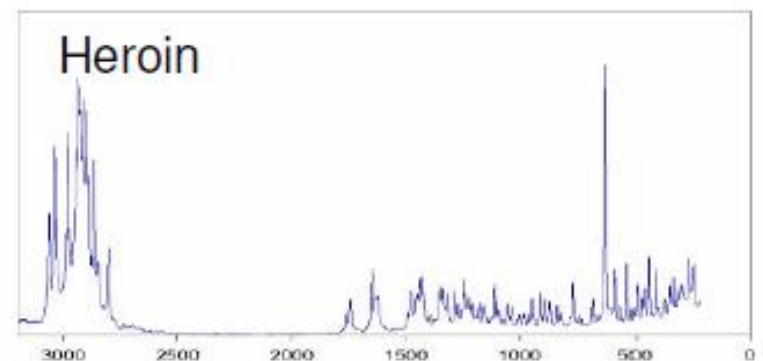
Methamphetamine



Cocaine

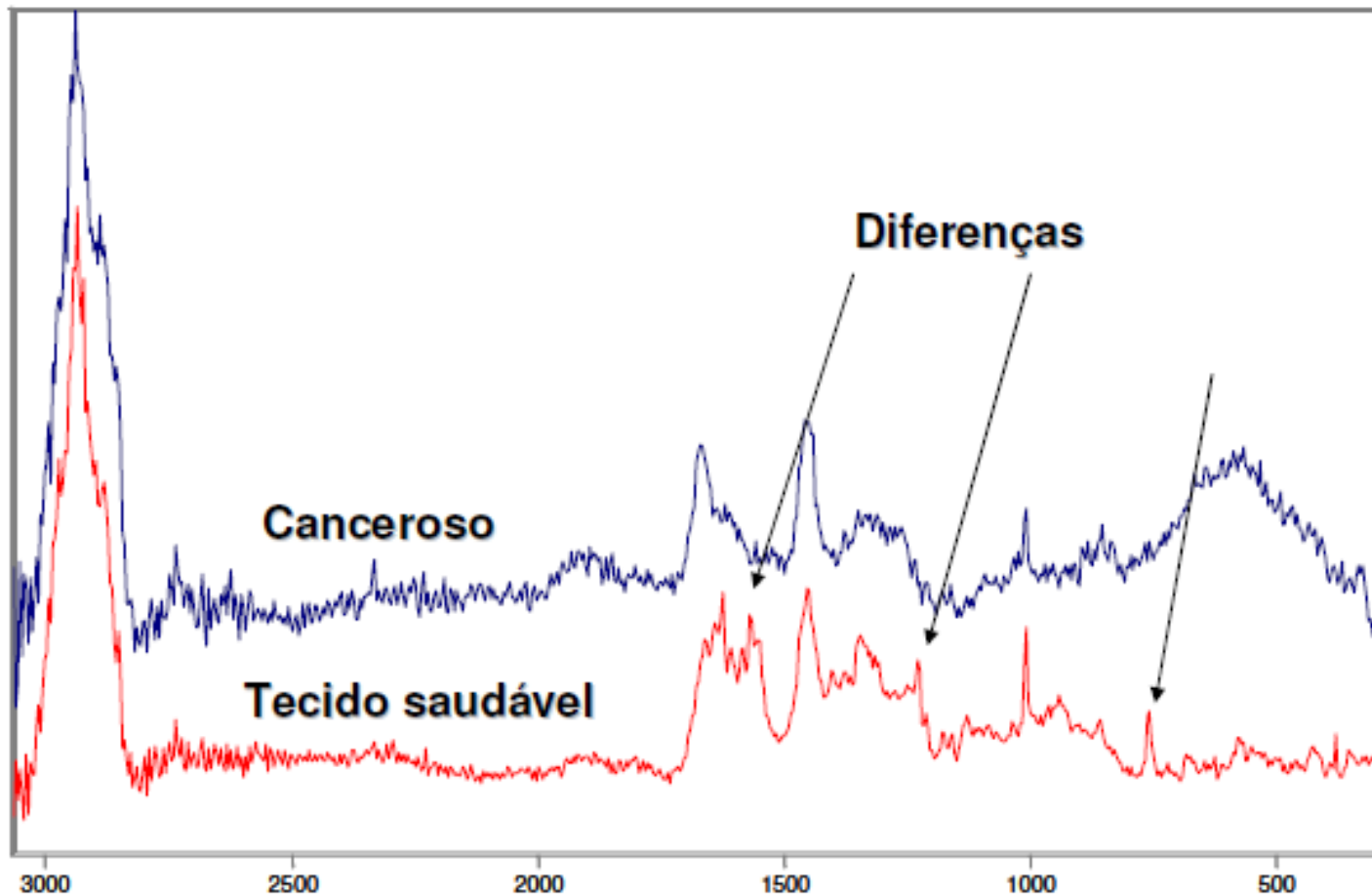


Heroin

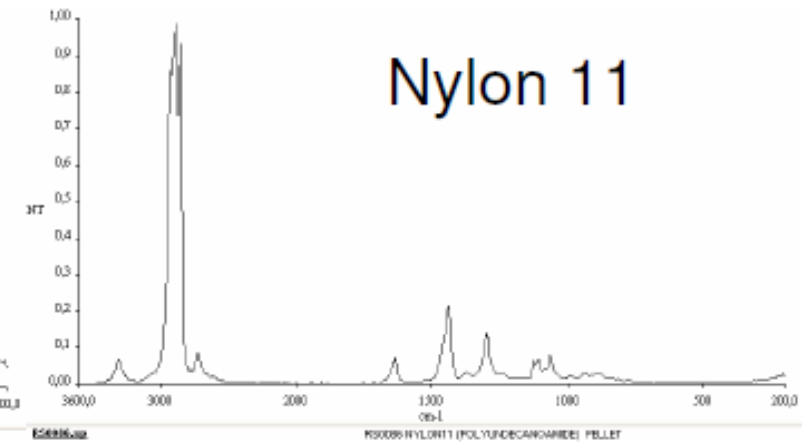
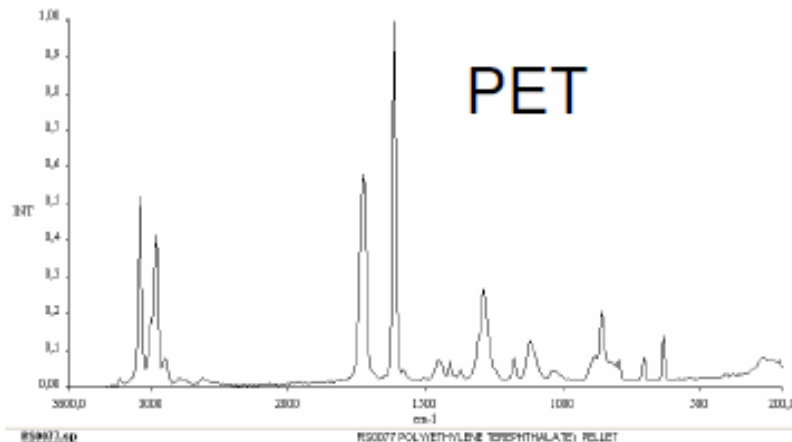
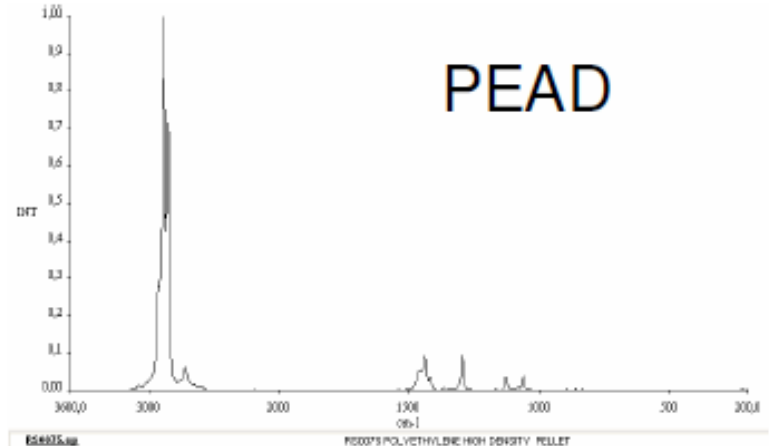
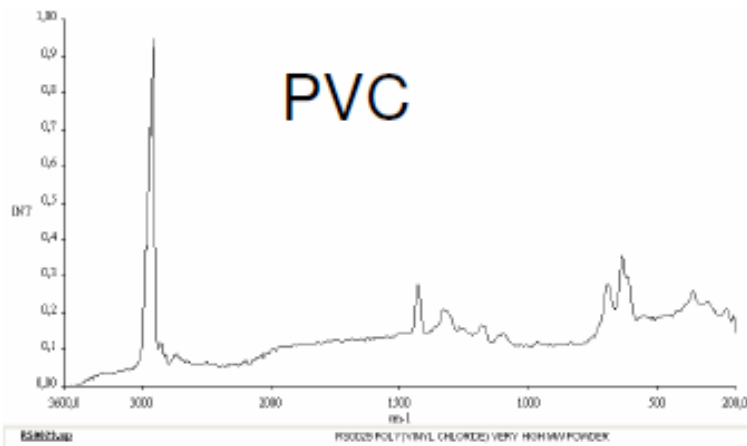




# Aplicações: tecido Canceroso



# Aplicações: Polímeros



- ▶ Cada espécie química, seja uma substância aglutinante, veículo ou verniz, pigmento, corante fornece um espectro que é como sua impressão digital

# Espectros Raman – Aplicações Pigmentos

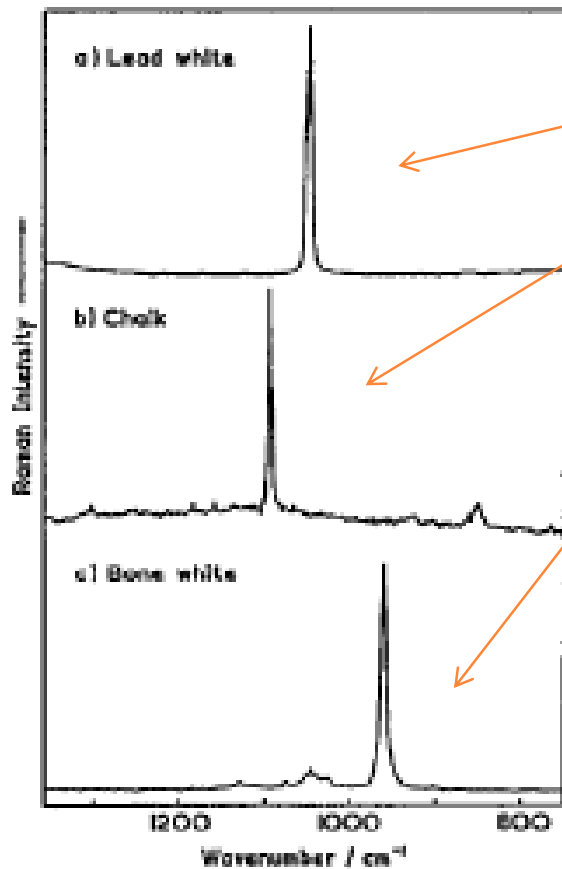
Wave number  $k=1/\lambda$

Lead white:  $k=1050 \text{ cm}^{-1}$  ( $\text{PbCO}_3$ )

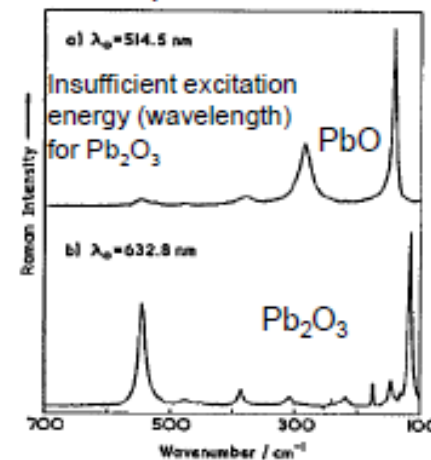
Chalk:  $k=1085 \text{ cm}^{-1}$  ( $\text{CaCO}_3$ )

Bone white:  $k=960 \text{ cm}^{-1}$  ( $\text{Ca}_3(\text{PO}_4)_2$ )

Red lead:  $k=226 \text{ cm}^{-1}, 313 \text{ cm}^{-1}, 390 \text{ cm}^{-1}, 549 \text{ cm}^{-1}$  ( $\text{Pb}_2\text{O}_3$ )



Raman spectrum of red lead

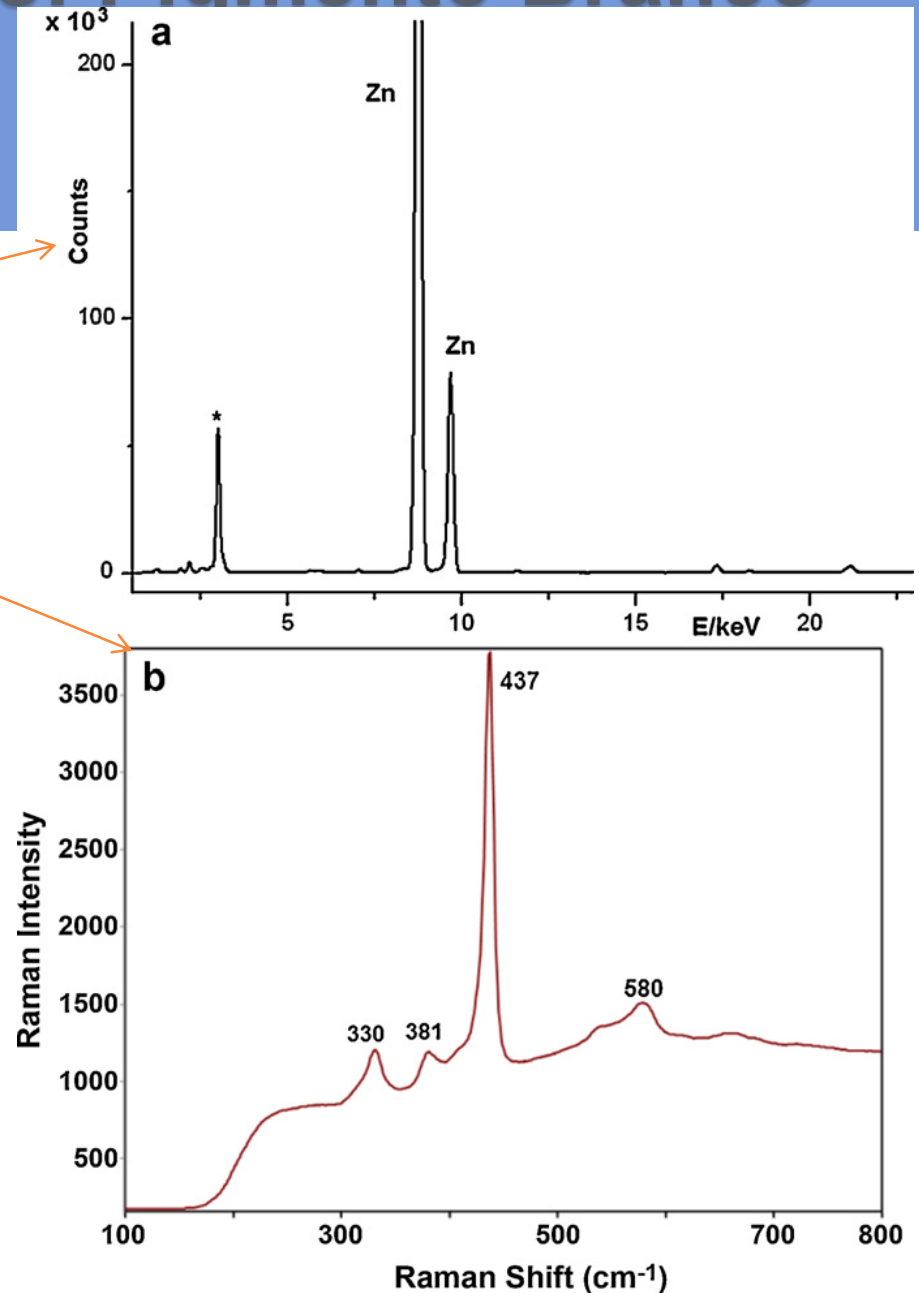


*Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation Lucia Burgio, Robin J.H. Clark, Spectrochimica Acta Part A 57 (2001) 1491*

# Aplicações: Pigmento Branco

▶ Acoplar as análises de ED-XRF com Raman

Espectros EDXRF e micro Raman do pigmento branco. O pico marcado com \* no espectro de EDXRF é devido ao equipamento e não pertence a amostra analisada



# Probing for yellow pigments

Historical yellow pigments: Yellow iron oxide

Orpiment

Lead tin antimony yellow

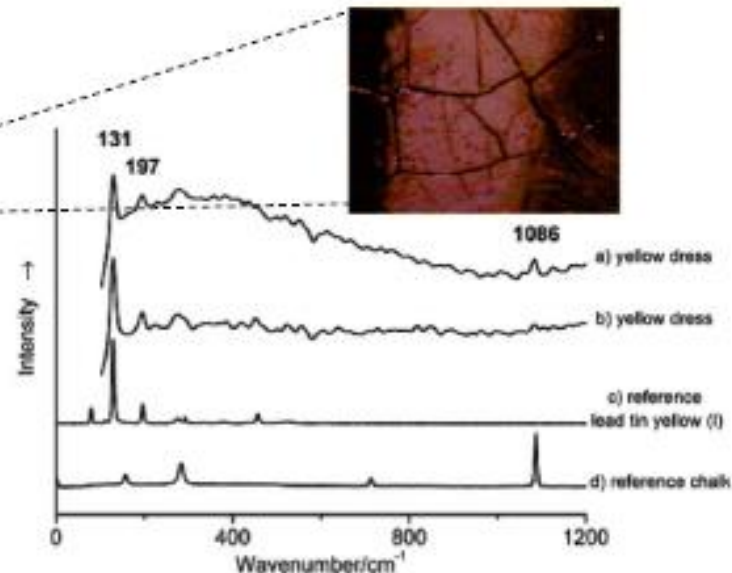
Lead antimonate

$\text{FeO}$

$\text{As}_2\text{S}_3$

$\text{Pb}_2\text{SnSbO}_{6.5}$

$\text{Pb}_2\text{Sb}_2\text{O}_7$



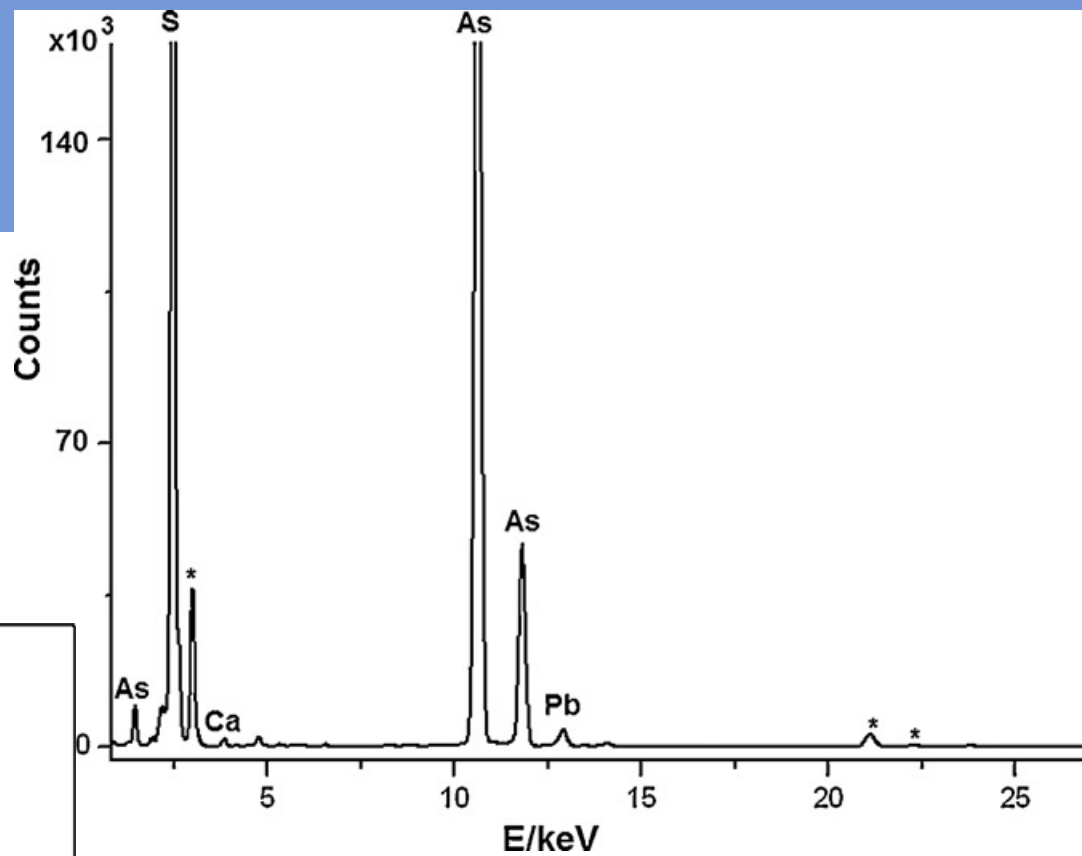
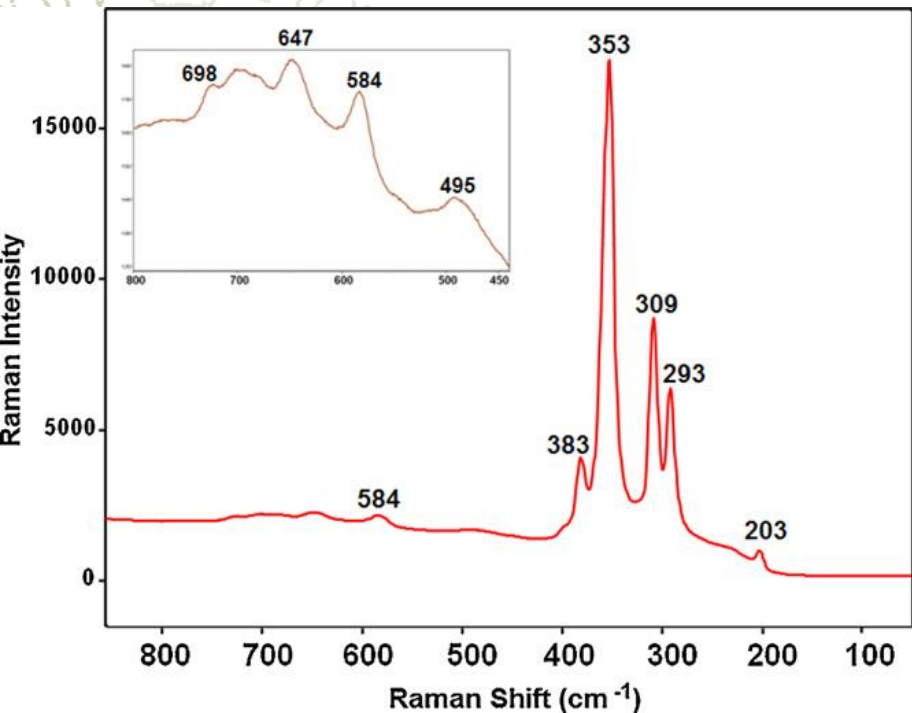
Clear identification of lead based yellow mixed with Calcite as used by Vermeer during his late period of painting ~1700 AD shortly before his untimely death in the age of 43 in 1705.

*L. Burgio et al. Anal Chem. 77, 1261 (2005)*

**Michael Wiescher** Department of Physics, University of Notre Dame, IN Updated: April 4, 2014

# Aplicações: Pigmento amarelo

▶ Acoplar as análises de ED-XRF com Raman

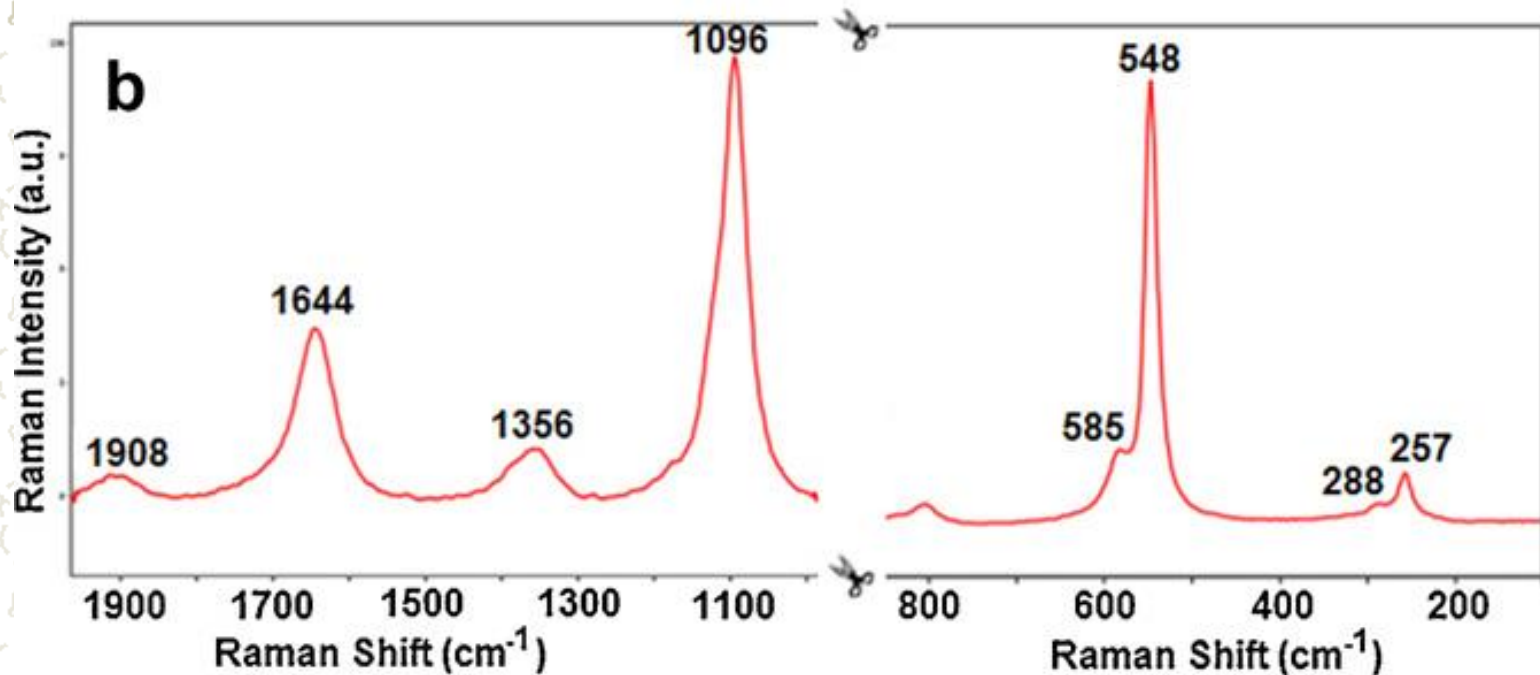


Orpiment: As<sub>2</sub>S<sub>3</sub>

# Aplicações: Pigmento azul

XRF: Si, Al, S

Raman: ultramarino ou lápis lazuli



|      |                                       |  |                                     |
|------|---------------------------------------|--|-------------------------------------|
| Blue | Azurite                               | $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$                          | Mineral                             |
|      | Cerulean blue                         | $\text{CoO} \cdot \text{SnO}_2$  | Synthetic, 19th century             |
|      | Cobalt blue                           | $\text{CoO} \cdot \text{Al}_2\text{O}_3$                               | Synthetic, 18th century             |
|      | Cobalt violet                         | $\text{Co}_3(\text{PO}_4)_2$   | Synthetic, 19th century             |
|      | Egyptian blue                         | $\text{CaO} \cdot \text{CuO} \cdot 4\text{SiO}_2$                      | Synthetic ca 3000 BC                |
|      | Han blue                              | $\text{BaCuSi}_4\text{O}_{10}$   | Mineral                             |
|      | Han purple                            | $\text{BaCuSi}_2\text{O}_6$  | Mineral                             |
|      | Lazurite/Ultramarine<br>/Lapis lazuli | $\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$    | Synthetic, 19th century<br>/Mineral |
|      | Manganese blue                        | $\text{BaSO}_4 \cdot \text{Ba}_3(\text{MnO}_4)_2$                      | 20th century                        |
|      | Posnjakite                            | $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ | Mineral                             |
|      | Prussian blue                         | $\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$                                | Synthetic, 18th century             |
|      | Smalt                                 | $\text{K}_2\text{O}, \text{SiO}_2, \text{CoO}$                         | 16th century                        |

# Azurite and Malachite

Different molecular components in complex molecules create certain Raman bands

$k=1000 \text{ cm}^{-1}$  vibration between anion and cation in salt

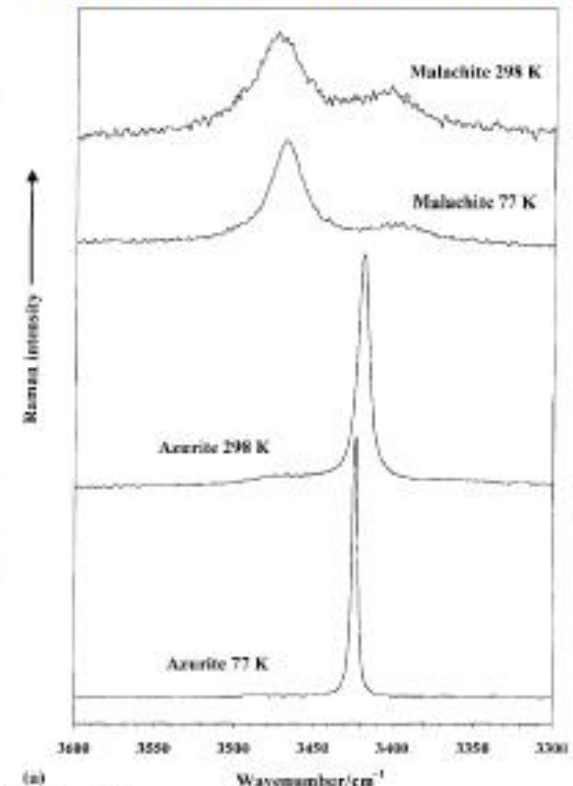
Lead white:  $k=1050 \text{ cm}^{-1}$  ( $\text{PbCO}_3$ )

Bone white:  $k=960 \text{ cm}^{-1}$  ( $\text{Ca}_3(\text{PO}_4)_2$ )



Malachite:  $\text{Cu}^{2+}_2(\text{CO}_3)(\text{OH})_2$

Azurite:  $\text{Cu}^{2+}_3(\text{CO}_3)_2(\text{OH})_2$



Generates vibration modes of three groups: O-H, C-O<sub>3</sub>, Cu-O

OH:  $k=952, 1035 \text{ cm}^{-1}$  (bending mode)  $3453, 3427 \text{ cm}^{-1}$  (stretching mode)

CO<sub>3</sub>:  $k=817, 837, 1090 \text{ cm}^{-1}, 1415, 1490 \text{ cm}^{-1}, 747, 769 \text{ cm}^{-1}$  (vibrational modes)

Cu-O:  $k=345, 455 \text{ cm}^{-1}$  (bending mode),  $k=400, 495 \text{ cm}^{-1}$  (stretching mode)



# Aplicações:

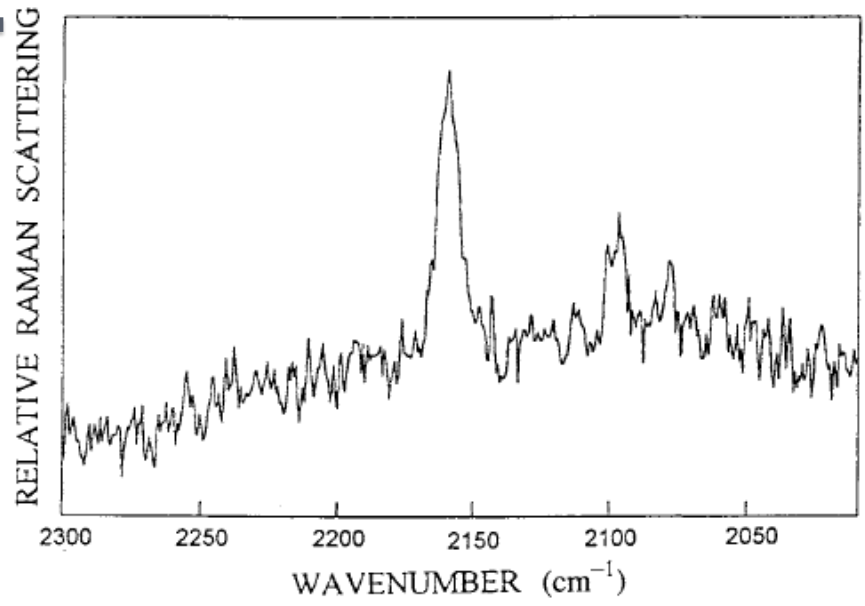
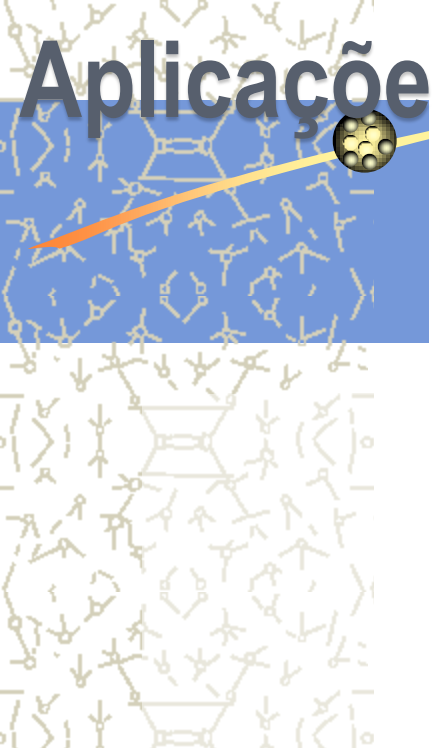


Figure 6 Raman spectrum of Prussian blue from a drawing by Constantin Guys (see text).

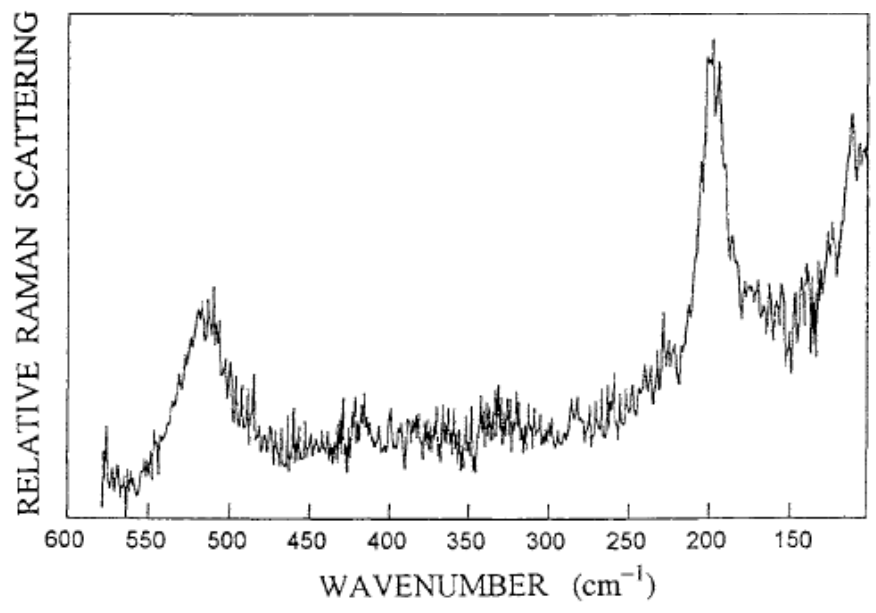


Figure 7 Raman spectrum of cobalt blue.

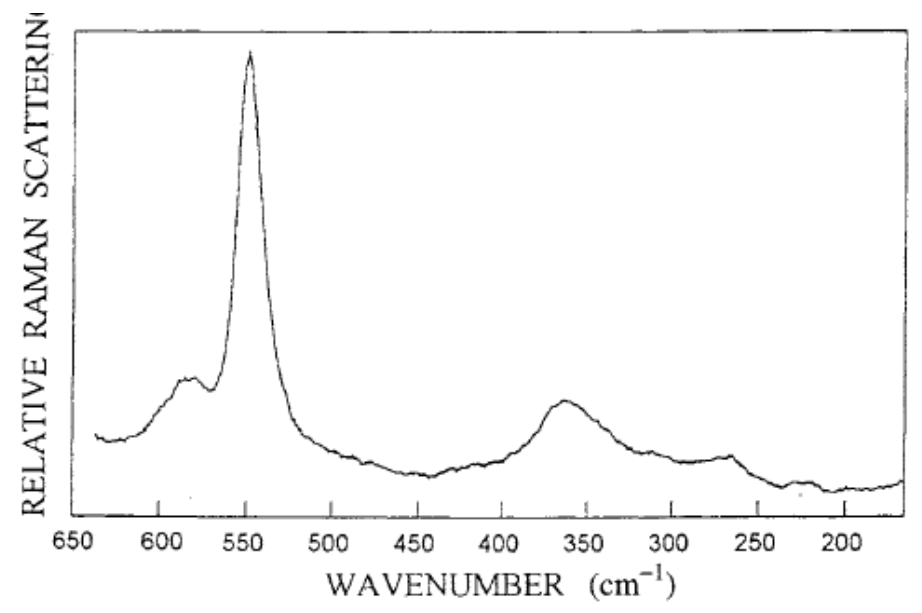


Figure 8 Raman spectrum of ultramarine blue.

# Aplicações: Pigmentos Picos Raman

| Pigmento             | Picos Raman (cm-1)   |              |
|----------------------|----------------------|--------------|
| Amarelo de Cadmio    | 302,610              | CdS          |
| Amarelo de Cromo     | 339,361,378,403,840, | PbCrO4       |
| Amarelo de Estrôncio | 337,858,866,891      | SrCrO4       |
| Anatase              | 145,396,514,637      | TiO2         |
| Azul da Prússia      | 2150                 | Século XVIII |
| Bário                | 987                  | BaSO4        |
| Branco de Zinco      | 437                  | ZnO          |
| Calcita              | 282,712,1086         |              |
| chalk                | 1086                 |              |
| gypsum               | 176,1010             |              |
| Orpiment             | 495,584,647,698      | As2S3        |
| Vermelho ocre        | 194,413              |              |

Ref.: Sevim Akyuza, Tanil Akyuza, Gulder Emreb, Ahmet Gulecb, Sait Basaran, "Pigment analyses of a portrait and paint box of Turkish artist Feyhaman Duran (1886–1970): The EDXRF, FT-IR and micro Raman spectroscopic studies". *Spectrochimica Acta Part A* 89 (2012) 74– 81.

# Aplicações: análise TiO<sub>2</sub>

Art, Jewelry and Forensic Science 433

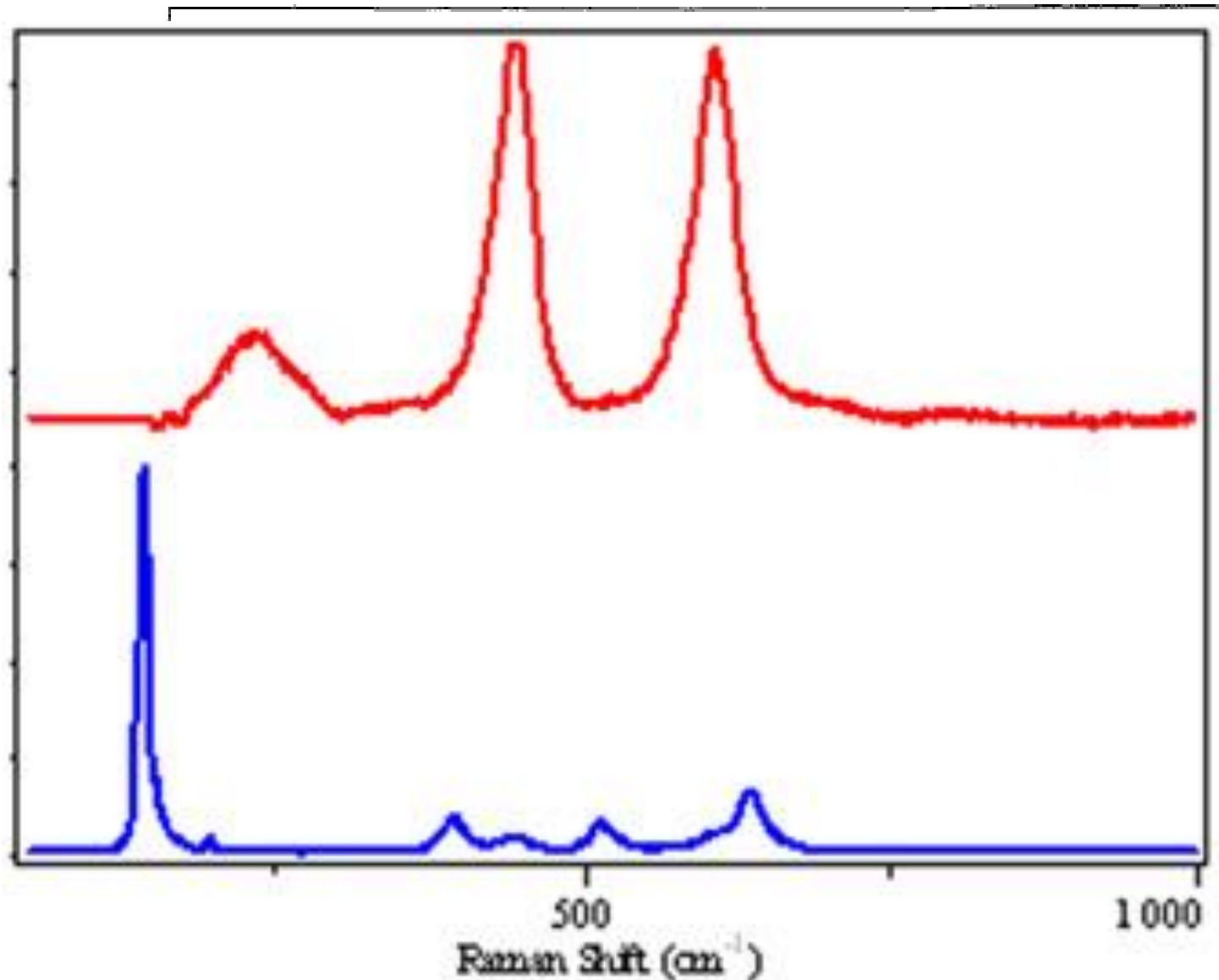
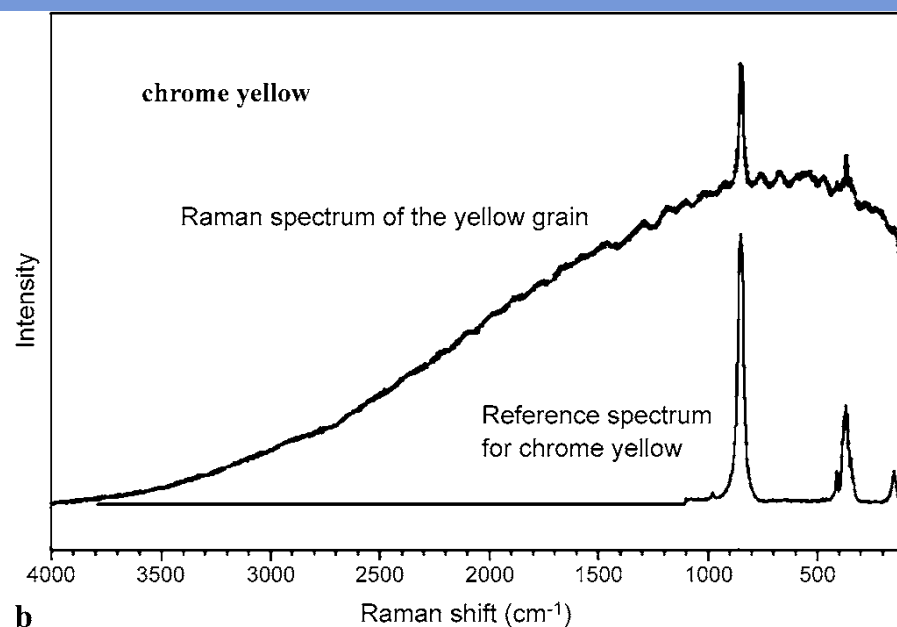
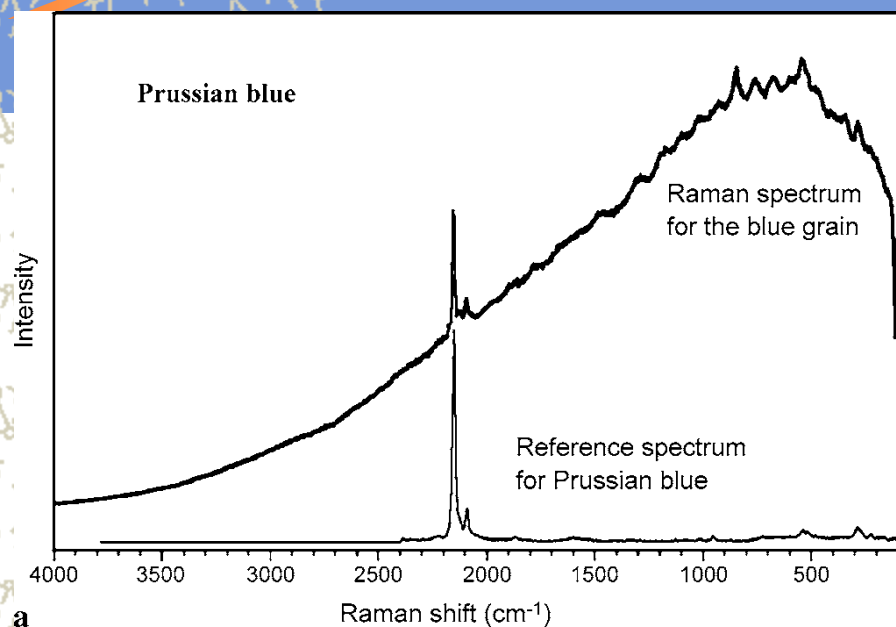


Figure 2. Raman spectra of TiO<sub>2</sub>: (a) anatase; (b) rutile.

# Exemplos de espectros Raman comparados com o sinal de fluorescência



Raman spectra taken on the (a) blue and (b) yellow grains, corresponding to the Prussian blue and chrome yellow pigments, respectively. Even though the background due to the fluorescence of the binding medium was rather high in both spectra, the characteristic Raman signal was attributed without difficulty to the appropriate pigments

# Experimental set-up during the analysis of the mediaeval manuscript Liber Floridus



A. Deneckere, M. De Reu, M. P. J. Martens, K. De Coene, B. Vekemans, L. Vincze, Ph. De Maeyer, P. Vandenabeele and L. Moens, *Spectrochim. Acta, Part A*, 2011, 80, 125

# Testing ink pigments of medieval monastery handwriting of letter R

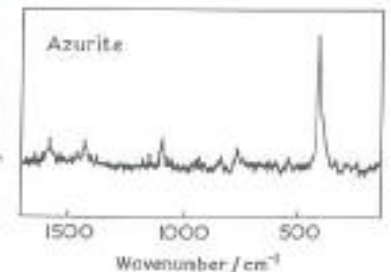
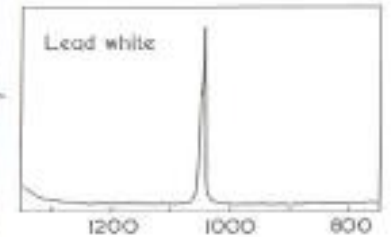
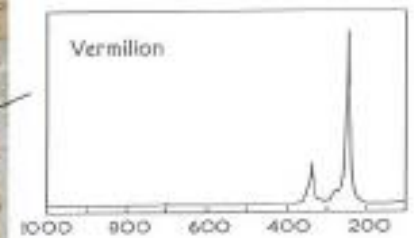
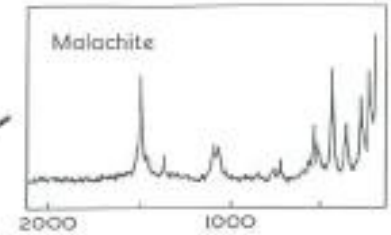
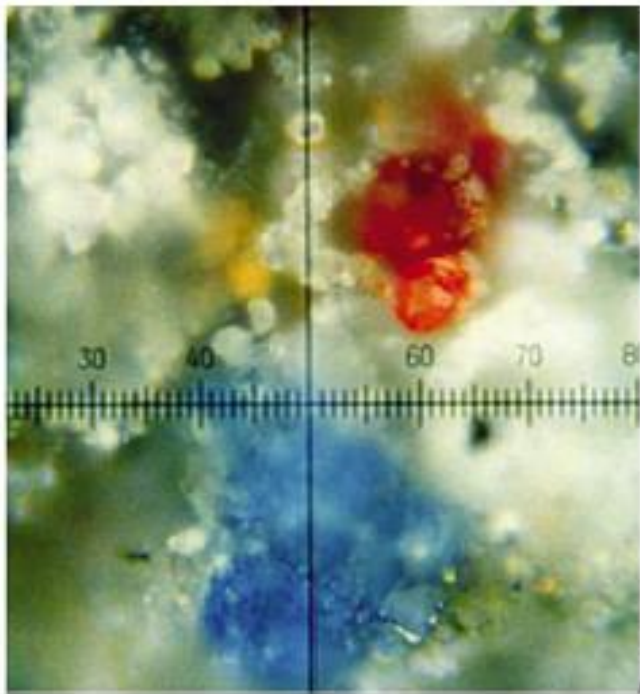
Lead white:  $k=1050\text{ cm}^{-1}$  ( $\text{PbCO}_3$ )

Malachite:  $(\text{Cu}^{2+}_2(\text{CO}_3)(\text{OH})_2)$  ( $k=1490\text{ cm}^{-1}$ )

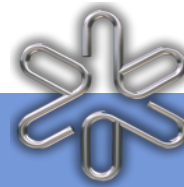
Azurite:  $(\text{Cu}^{2+}_3(\text{CO}_3)_2(\text{OH})_2)$  ( $k=495\text{ cm}^{-1}$ )

Vermillion:  $k=253\text{ cm}^{-1}$ ,  $285\text{ cm}^{-1}$ ,  $343\text{ cm}^{-1}$  ( $\text{HgS}$ ) (cinnabar)

Minium:  $k=226\text{ cm}^{-1}$ ,  $313\text{ cm}^{-1}$ ,  $390\text{ cm}^{-1}$ ,  $549\text{ cm}^{-1}$  ( $\text{Pb}_2\text{O}_3$ )

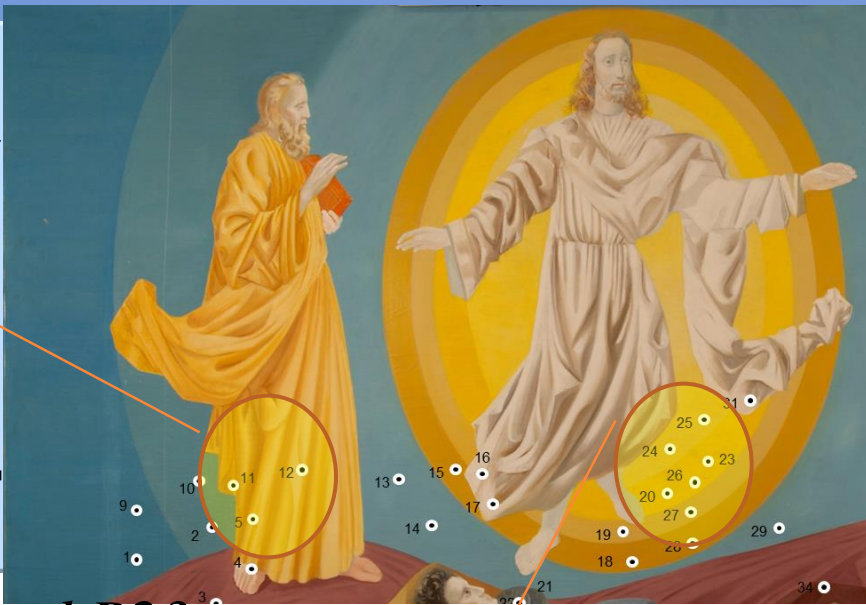
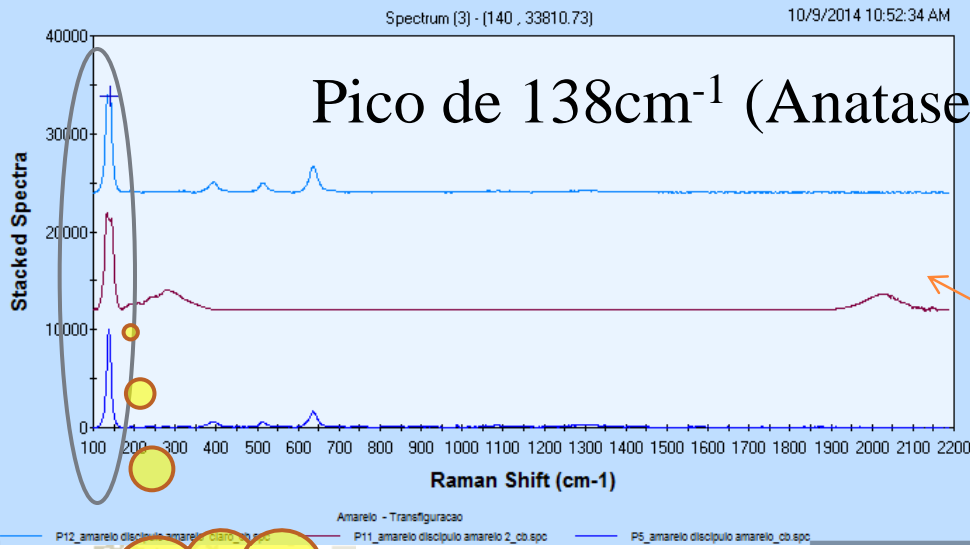


*Best et al. Endeavour, New Series 16 (1992) 66-73*



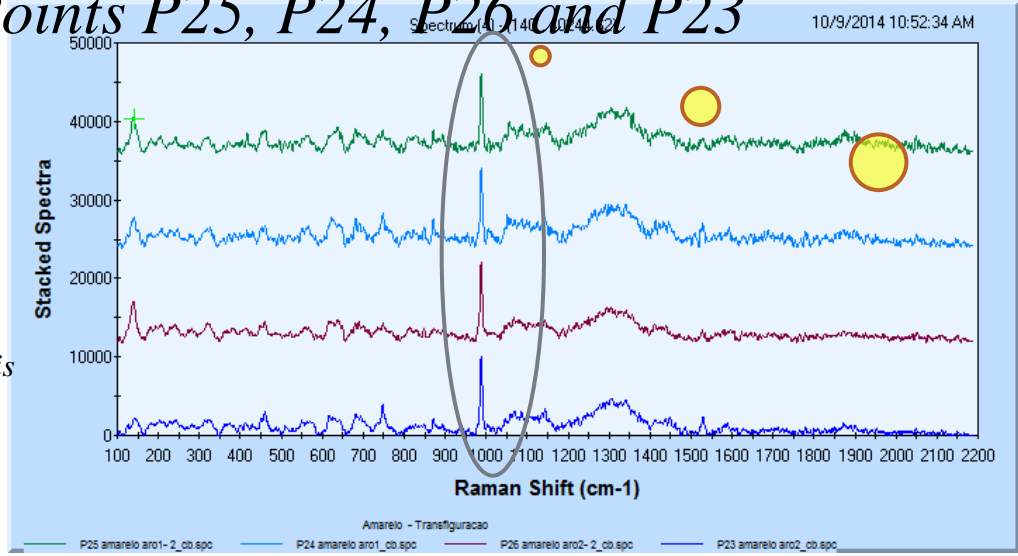
## Raman RESULTADOS – PONTOS AMARELOS

Pontos P12, P11 and P5



**Pequena quantidade de Ti em pontos amarelos com XRF apresentam alta quantidade de anatase nos pontos Raman**

Points P25, P24, P26 and P23



**Pico de 988 cm<sup>-1</sup> Lithopone (ZnS, BaSO<sub>4</sub>). Branco de Chumbo, pico em 1050 cm<sup>-1</sup> (pouca quantidade)**

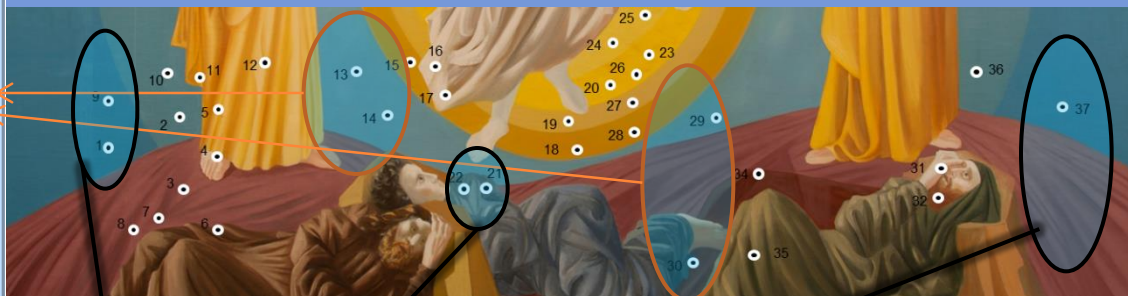
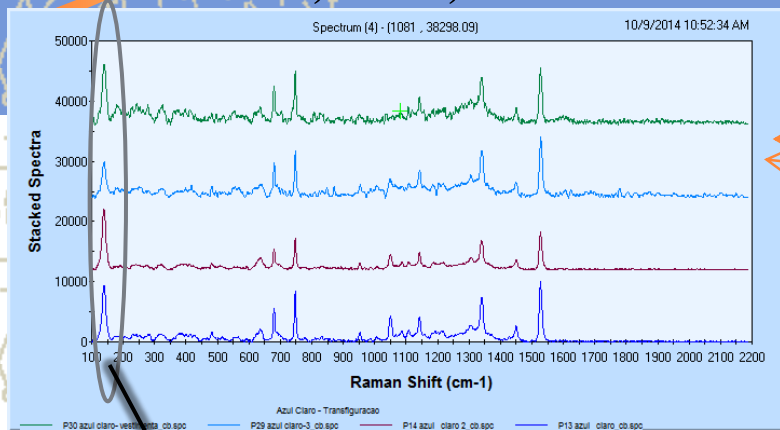
**Sem a presença do pico característico do pigmento amarelo (XRF amarelo de Cd)**

TiO<sub>2</sub> Anatase, linhas principais 138, 390, 512 e 634cm<sup>-1</sup>. (<http://cameo.mfa.org/>)

# Obra: "Transfiguração" de Candido Portinari (1,99x2,99 m)

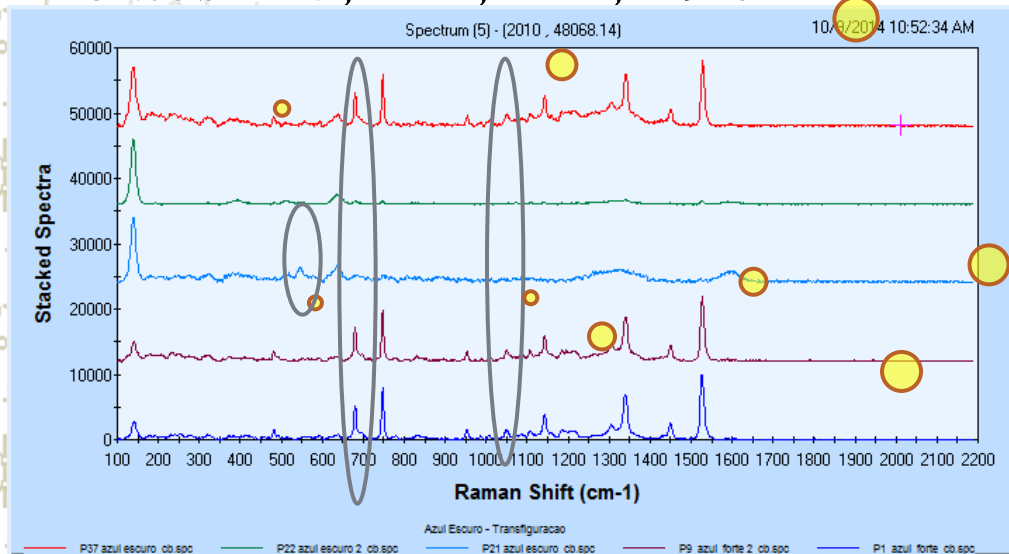
## Resultados Raman – pontos BLUE POINTS

### Pontos P30, P29, P14 e P13



Pico de  $138\text{cm}^{-1}$  (Anatase –  $\text{TiO}_2$ ).

### Pontos P37, P22, P21, P9 e P1



Pico de  $670\text{cm}^{-1}$   
Azul Cerulean ( $\text{CoO.SnO}_2$ ) e  
talves outros picos :  $750, 1140,$   
 $1340$  and  $1530\text{cm}^{-1}$

Pico de  $1050\text{cm}^{-1}$   
Branco de chumbo (pouca  
quantidade)

peak at  $546$  and  $1090\text{cm}^{-1}$   
Ultramar Blue



# Outras Aplicações:

## (i) biological:

blood, semen, urine

skin

hair (natural or textiles), feathers

vegetal residues, e.g. fibers, wood, paper

## (ii) mineral:

gems and other geological specimens

metallic residues

## (iii) synthetic materials:

explosives and propellants

plastics and composites

paints

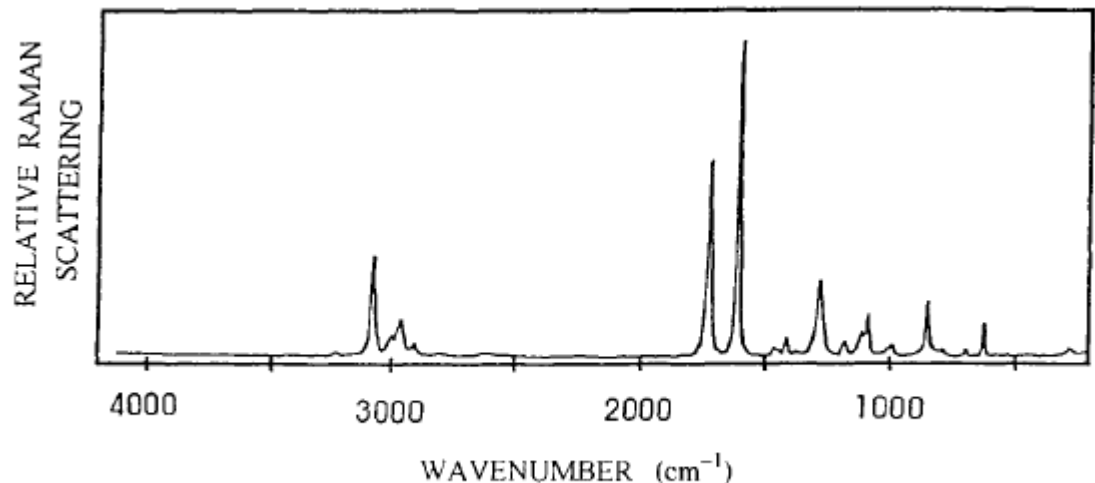


Figure 15 Raman spectrum of a polyester ( $\lambda_0 = 514.5$  nm; laser power = 10 mW).

# Gemas



A aplicação da espectroscopia Raman em gemologia foi revisada por: Bersani e Lottici, que fizeram revisão geral das diferentes pedras preciosas que foram examinadas por Raman. Smith realizou uma revisão ampla de uso de Raman para identificar minerais no contexto arqueométrico, já que a espectroscopia de Raman é um método espectroscópico molecular que pode diferenciar entre estruturas cristalinas e deste modo é uma excelente ferramenta para a identificação de pedra preciosas.

D. Bersani and P. P. Lottici, *Anal. Bioanal. Chem.*, 2010, 397, 2631.

P. Vandenabeele and L. Moens, *Anal. Bioanal. Chem.*, 2006, 385, 209.

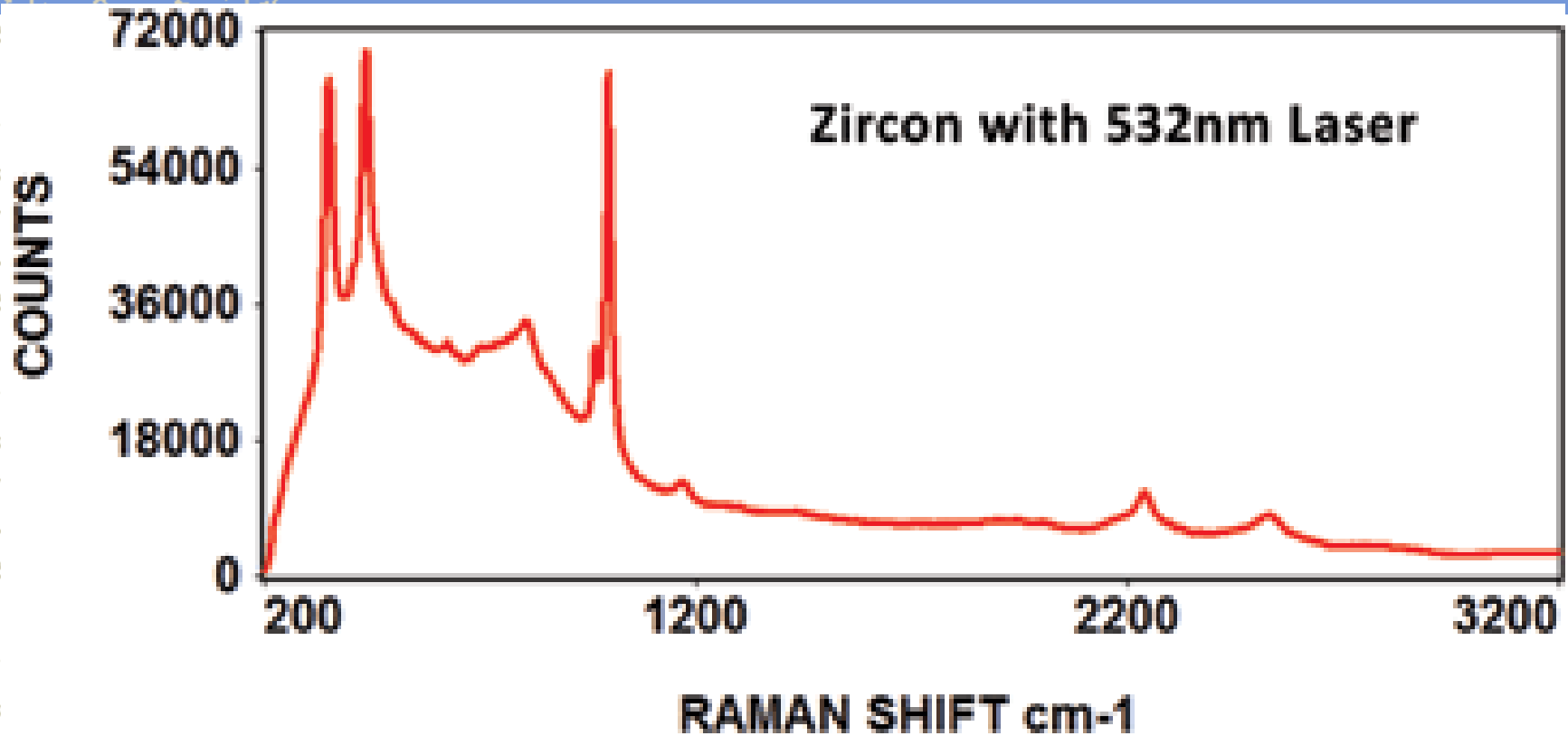
I. Reiche, S. Pages-Camagna and L. Lambacher, *J. Raman Spectrosc.*, 2004, 35, 719.

| materiais   | Raman                       |
|---|-----------------------------|
| Diamantes   | 1332 $\text{cm}^{-1}$       |
| Rubi e safira ( $\text{Al}_2\text{O}_3$ )                       | 418 e 644 $\text{cm}^{-1}$  |
| Esmeraldas ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ) | 687 e 1070 $\text{cm}^{-1}$ |

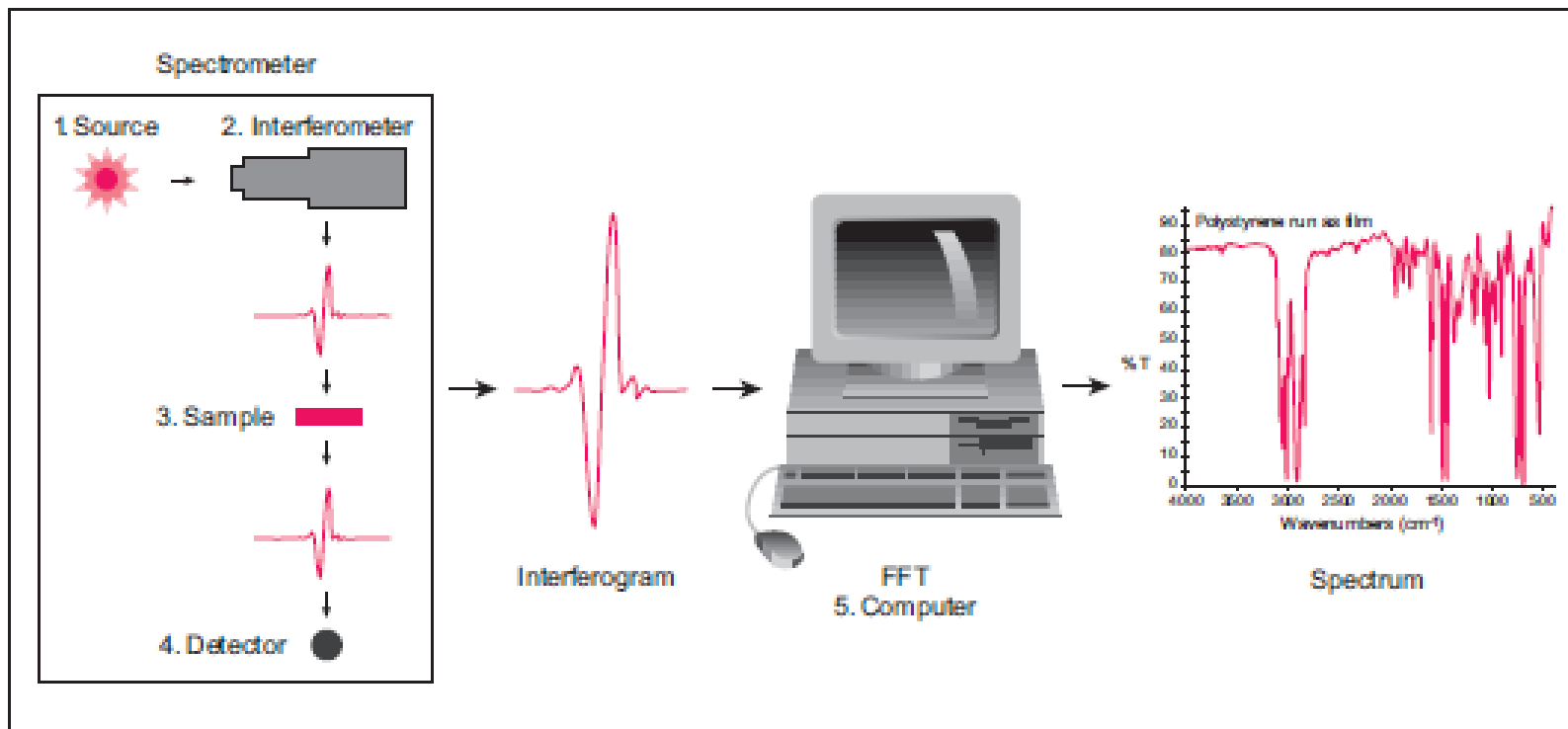
**Applications in Art, Jewelry and Forensic Science**

Claude Coupry and Didier Brissaud

## Exemplos espectros Raman da Zirconia



# FTIR – Espectroscopia de Infravermelho por transformada de Fourier



# FTIR – Brucker modo reflexão

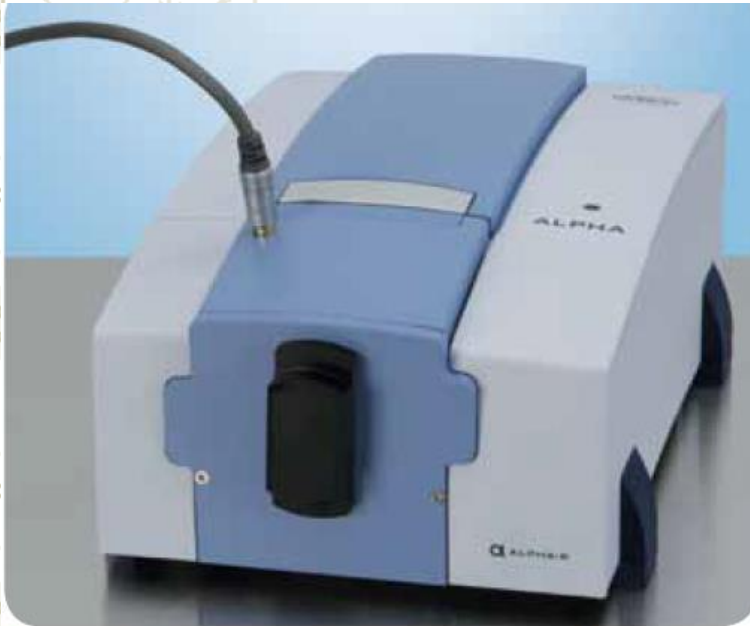


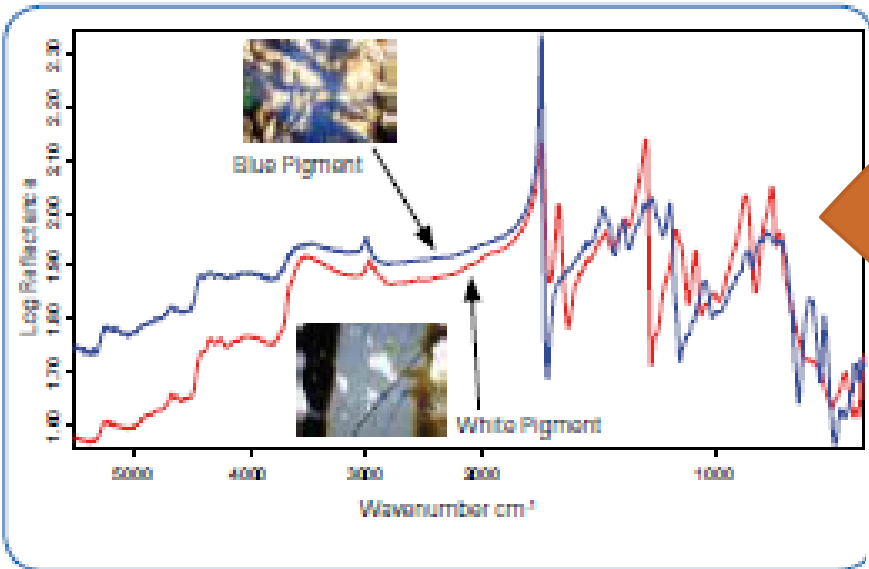
Figure 1: ALPHA-R with forward looking reflection unit including video.



Figure 2: Nottetempo by Mario Schifano with a tripod mounted ALPHA-R in the front.

espectroscopia FTIR para análise de superfície da  
pintura de Mario Schifano (Centro Studi e Archivo  
della Comunicazione – Parma)

# Resultado FTIR



**KKT**  
Transformação Kramers  
Kronig

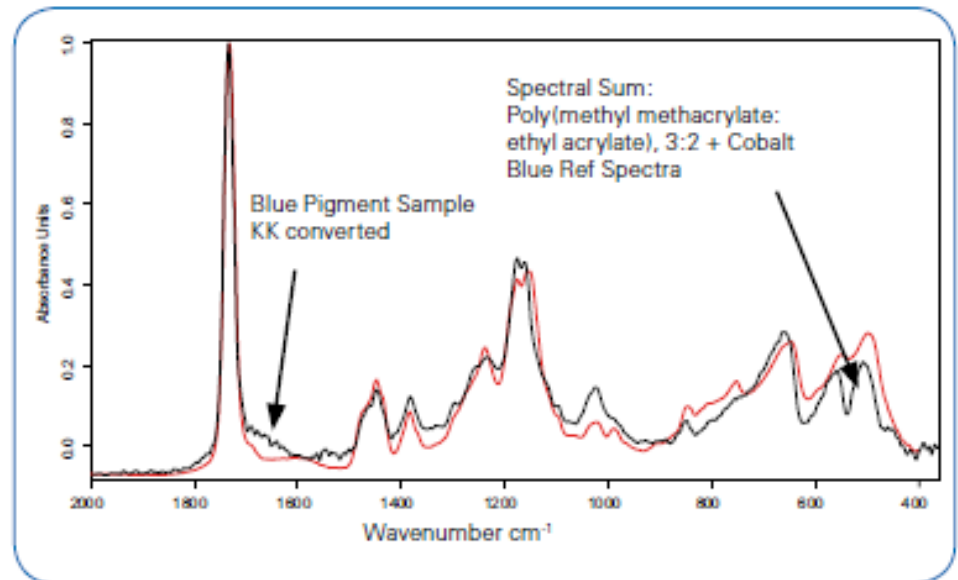


Figure 5: KKT transformed sample spectrum of a blue pigmented area (black curve) and sum spectrum of different reference spectra (red curve).

# FTIR

Figure 6: Polittico di Giotto with a tripod mounted ALPHA-R and a laptop PC.

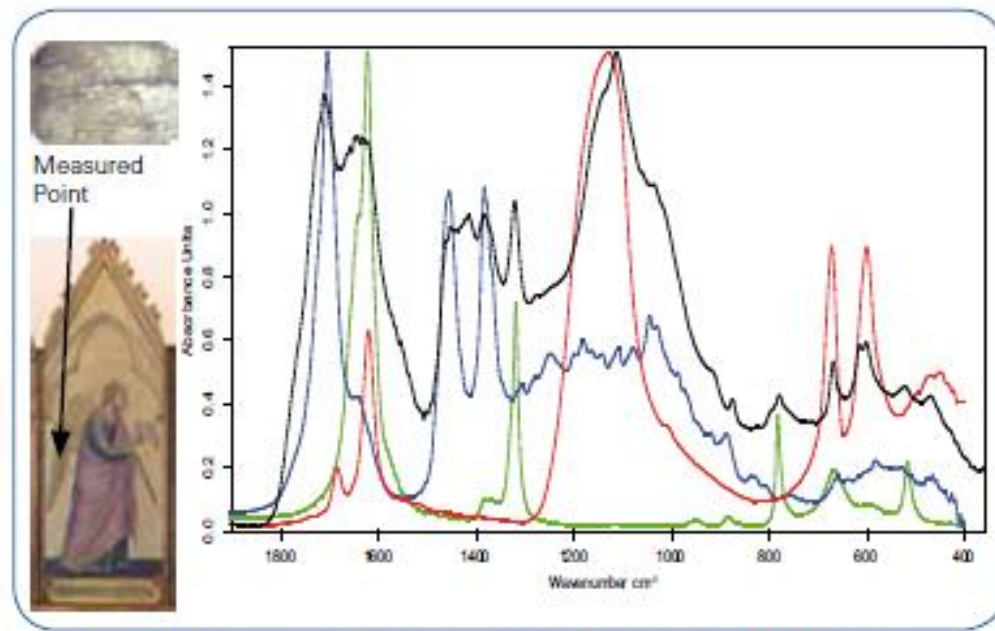


Figure 7: Detail of panel and video image of the measurement point (left). Right: Sample spectrum (black) and reference spectra of terpenic varnish (blue), calcium sulfate (red) and calcium oxalate (green).

# DIFRAÇÃO

• Condições que permitam observar o fenômeno de difração:

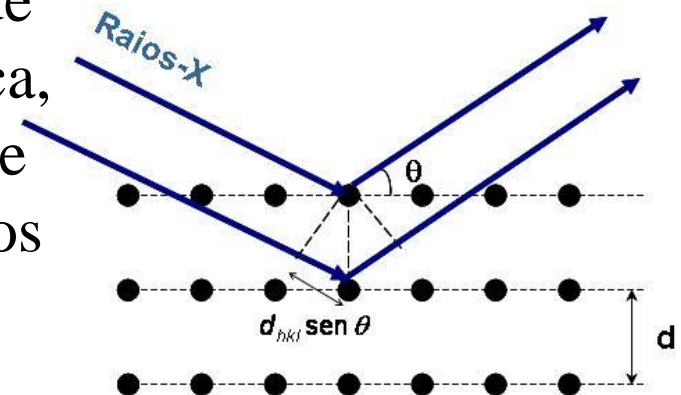
- Arranjo experimental
- Radiação incidente
- Arranjo periódico de átomos

$$\text{Lei de Bragg: } m\lambda = 2d \sin\theta$$

$$\text{Resolução: } m\lambda = 2d \sin\theta \longrightarrow m\Delta\lambda = 2d \cos\theta \Delta\theta \longrightarrow \Delta\theta/\Delta\lambda = m/(2d\cos\theta)$$

Ocorre melhor dispersão quando o ângulo  $\theta$  é grande e o valor de  $2d$  é um pouco maior que  $\lambda$  ( $d$  pequeno). A resolução é pior para ângulos  $\theta$  pequenos.

**DIFRAÇÃO DE RAIOS X** Fenômeno de espalhamento da radiação eletromagnética, provocada pela interação entre o feixe de raios-X incidente e os elétrons dos átomos componentes de um material.





# INTERAÇÃO DOS RAIOS X COM OS CRISTAIS

## DIFRAÇÃO NÃO É REFLEXÃO

- O feixe difratado contém contribuições do espalhamento de todos os átomos do cristal que estão no caminho do feixe incidente. A reflexão da luz visível ocorre apenas numa fina camada superficial.
- A difração de raios X monocromáticos ocorre apenas em ângulos que satisfazem a Lei de Bragg. A reflexão de luz visível ocorre para qualquer ângulo de incidência.
- A reflexão de luz visível por um bom espelho é ~100% eficiente. A intensidade dos raios X difratados  $\ll$  intensidade  $I_0$ .

# ORDENS DE DIFRAÇÃO

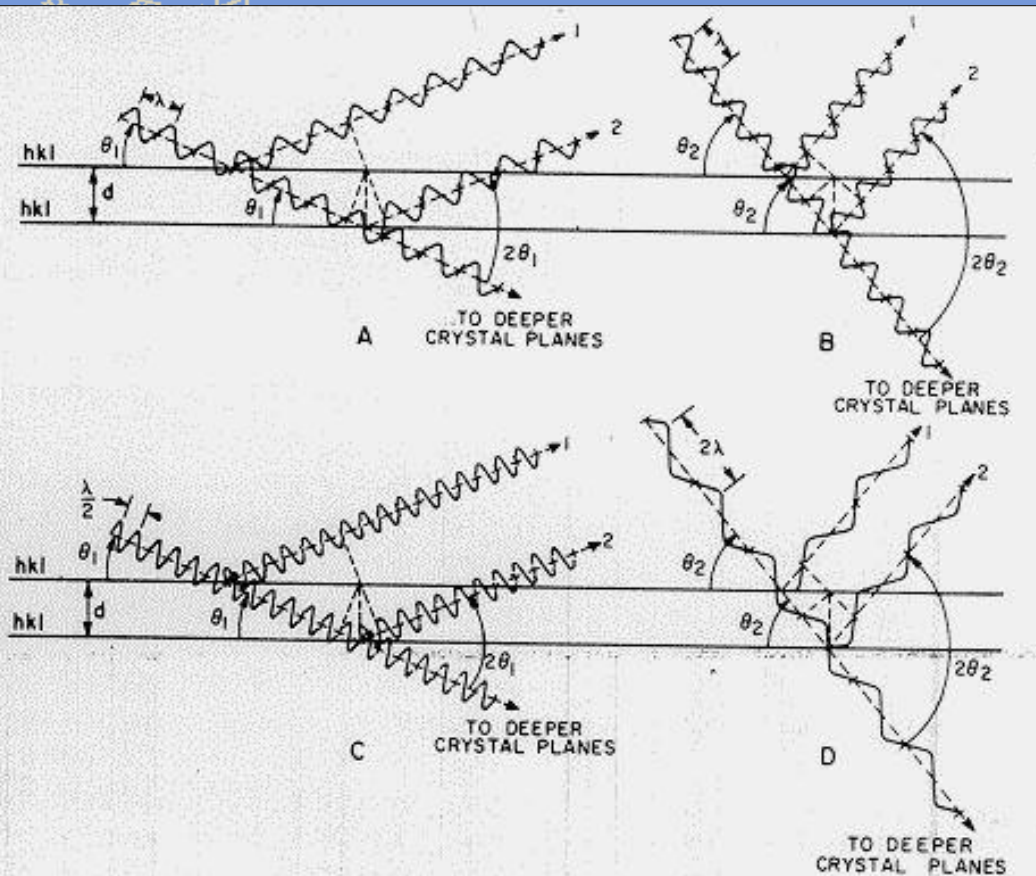


FIG. 2.15. Origin of diffraction orders.

**A:** Primeira ordem de difração  
comprimento de onda  $\lambda$  em  $\theta_1$   
diferença de caminho =  $\lambda$

**B:** Segunda ordem de difração  
comprimento de onda  $\lambda$  em  $\theta_2$   
diferença de caminho =  $2\lambda$

**C:** Segunda ordem de difração  
comprimento de onda  $\lambda/2$  em  $\theta_1$   
diferença de caminho =  $\lambda$  (A)

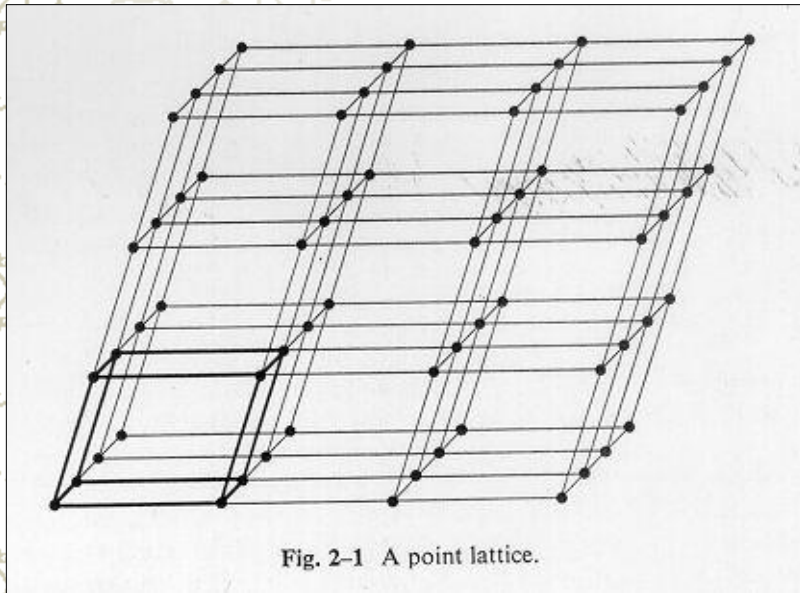
**D:** Primeira ordem de difração  
comprimento de onda  $2\lambda$  at  $\theta_2$   
diferença de caminho =  $2\lambda$  (B)

- Mesmo comprimento de onda difrata o mesmo  $d_{hkl}$  em ângulos diferentes.

- Diferentes comprimentos de onda difratam no mesmo ângulo de Bragg.

# Geometria do estado cristalino

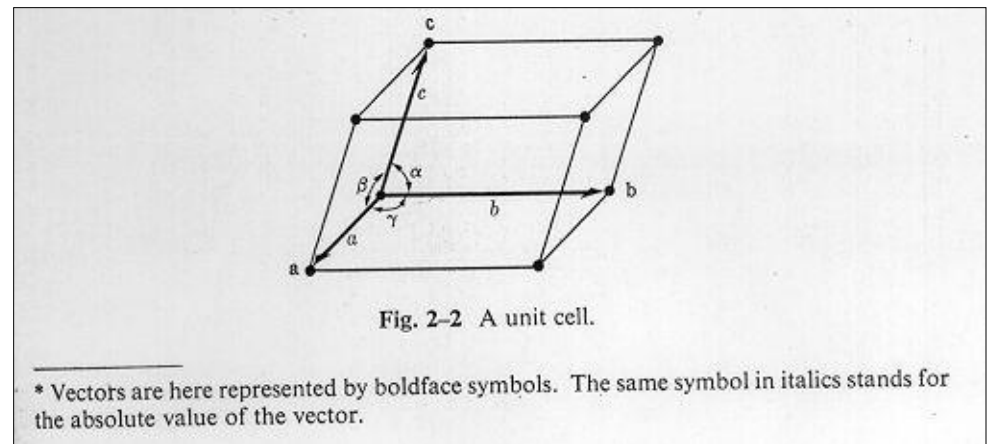
Cristal: arranjo periódico de átomos



Parâmetros de rede

$a, b, c$  = eixos cristalográficos

$\alpha, \beta, \gamma$  = ângulos entre os eixos



# Difração de raios X

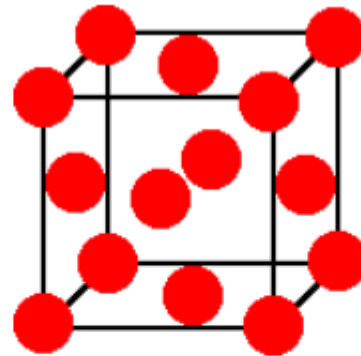


Fig. 5.11

Nessa estrutura, os átomos funcionam como obstáculos, ou centros de espalhamento dos raios X. Os cristais são formados quando bilhões e bilhões de estruturas idênticas são colocadas lado a lado. Desse modo, formam-se famílias de planos atômicos, separadas por distâncias inferiores a 1 nm.

Pode-se utilizar a difração de raios X para identificar novos materiais através do espalhamento dos raios X pelos átomos do cristal e determinar a distância interatômica do material, e deste modo identificar o material  
1953 usando esta técnica foi identificado o DNA

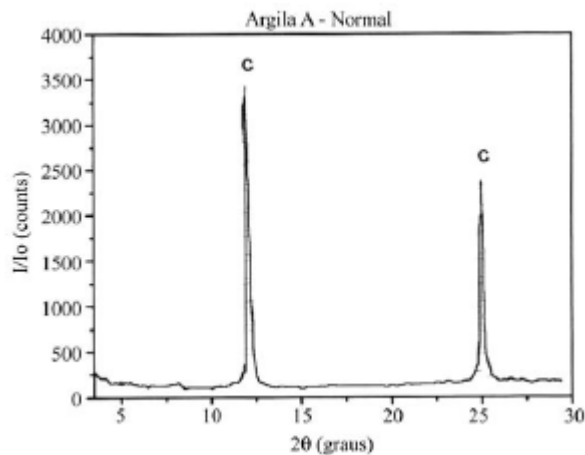
# Determinação de argilominerais por XRD

## Determinação de fases cristalinas em materiais cerâmicos

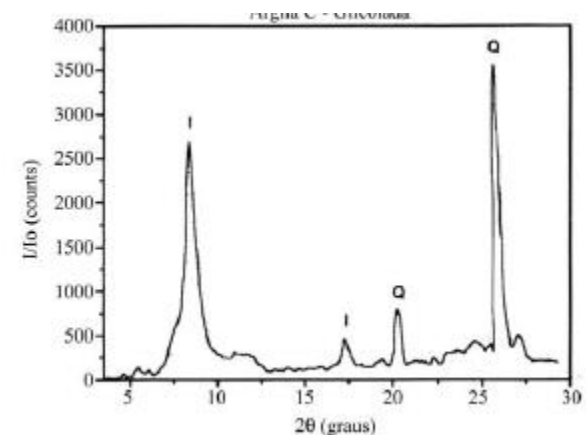
Tabela I - Distâncias interplanares características [1].  
[Table I: Interplanar distance [1].]

| Distância Interplanar (Å) (pico principal) | Distância Interplanar (Å) (picos secundários) | Argilomineral           |
|--|---|-------------------------|
| 7  | 3,58  | Caulinita               |
| 10   | 5,0 e 3,33                                    | Ilita                   |
| 14   | 7,0; 4,7 e 3,5                                | Clorita                 |
| 14   | 7,0; 4,7 e 3,5                                | Clorita expansível      |
| 12 ou 14                                   | 5,1 e 3,5                                     | Montmorilonita-12 ou 14 |
| 14   |   | Vermiculita             |

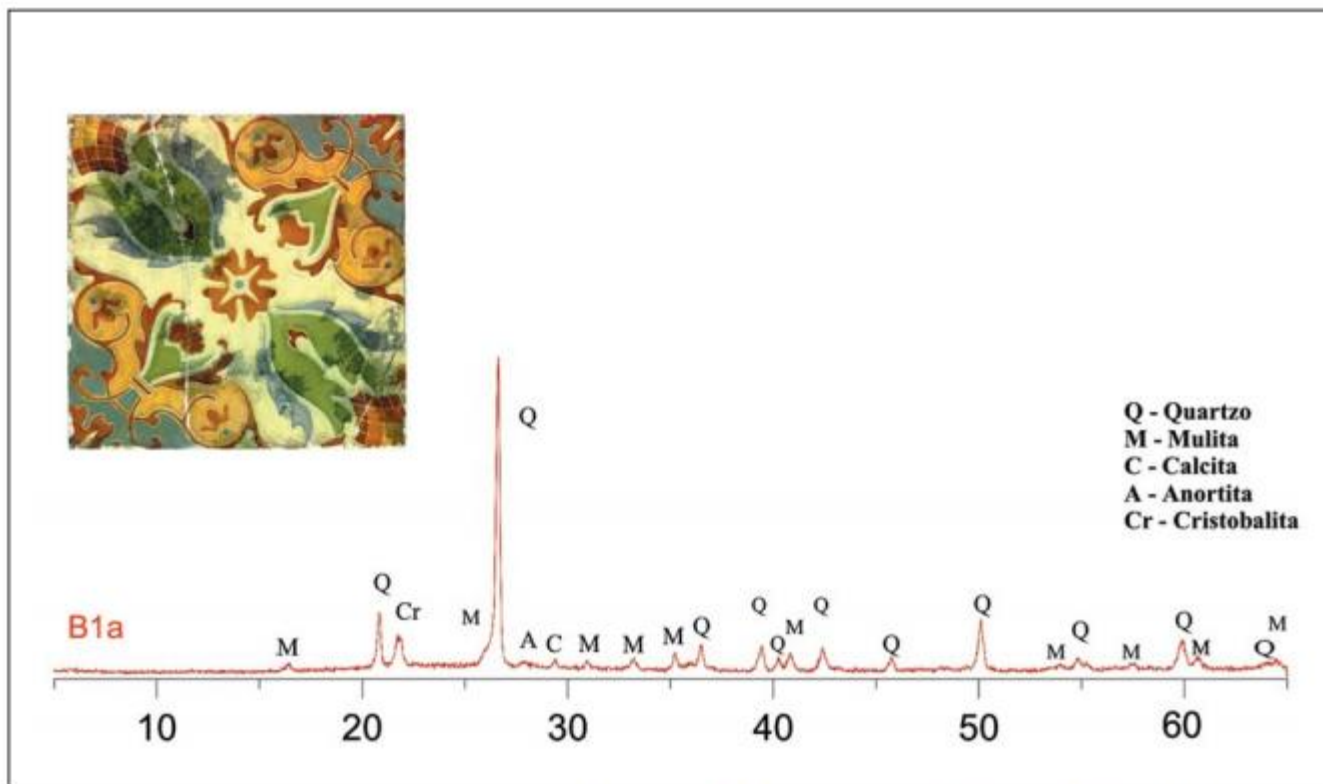
Difratograma de uma argila identificando a Caulinita (C)



Difratograma de uma argila identificando o Quartzo (Q) e ilita (I)



# Caracterização mineralógica de azulejos século XVI, XVII e XIX



**Figura 1** - Difratoograma da amostra B1-A, com a imagem do azulejo analisado. Essa amostra de azulejo é do século XIX, da Fábrica Villeroy e Boch, Alemanha.

# CARACTERIZAÇÃO MINERALÓGICA DE AZULEJOS SÉCULO XVI, XVII E XIX

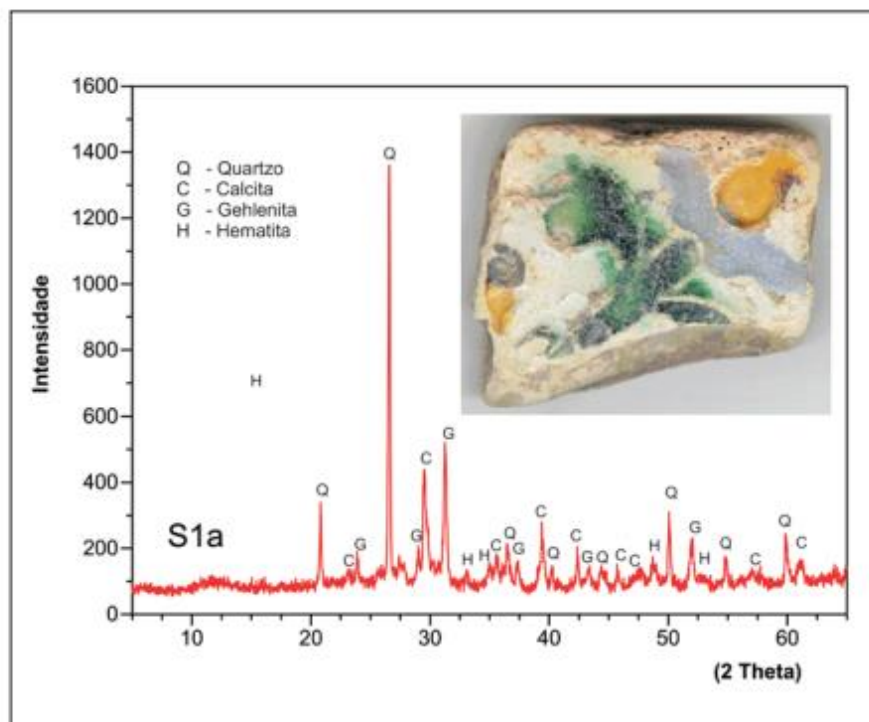


Figura 2 - Difratoograma de raios X da amostra S1-A, com a imagem do azulejo analisado, que é um fragmento de azulejo hispano-mourisco.

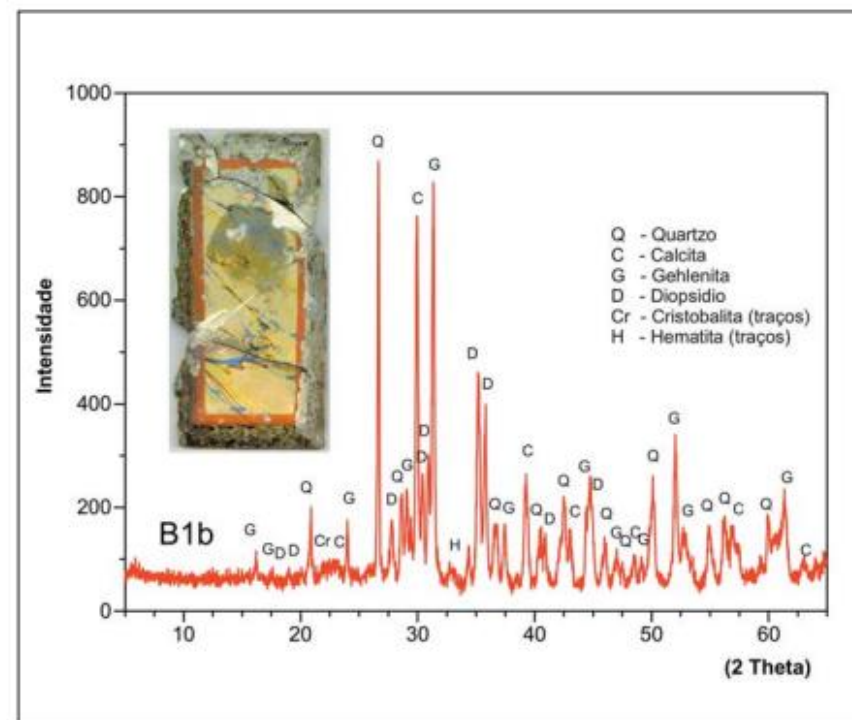


Figura 3 - Difratoograma de raios X da amostra B1-B, com a imagem do azulejo analisado, do século XIX e de origem portuguesa.

# Equipamento de XRD Brucker

<https://www.bruker.com>

## Applications

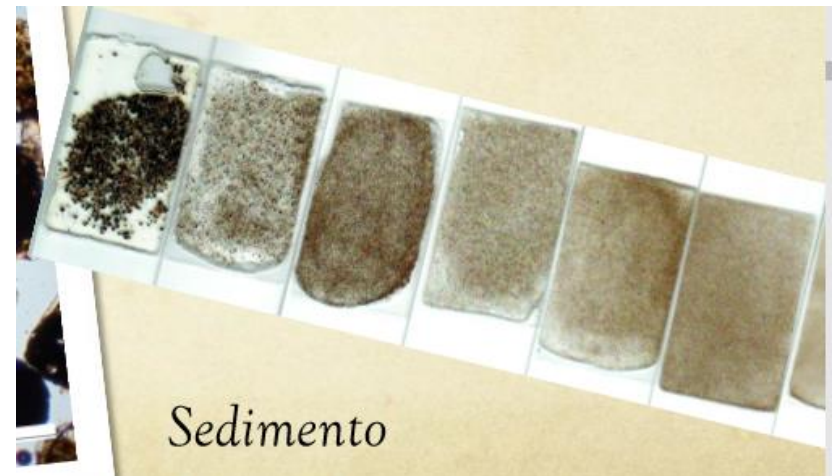
- Crystalline phase identification
- Crystalline phase quantification
- % crystallinity
- Crystallite size determination
- Crystal structure analysis
- Crystal orientation
- Texture and preferred orientation
- Microstrain
- Residual stress
- Depth profiling
- Polymorph screening
- High temperature
- Low temperature
- Humidity
- Phase transition
- Nanoparticles





# Microscopia petrográfica

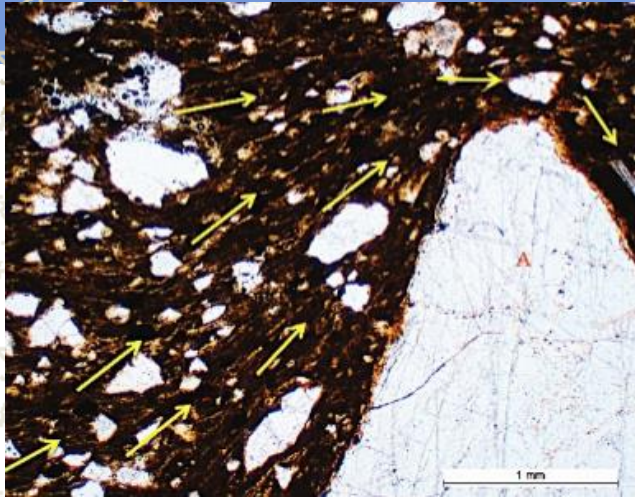
Faz uso da interação de um feixe de luz polarizado com uma fina seção da amostra a ser analisada, por meio de uma lâmina de seção delgada da cerâmica, ou matéria-prima argilosa sobre uma lâmina.



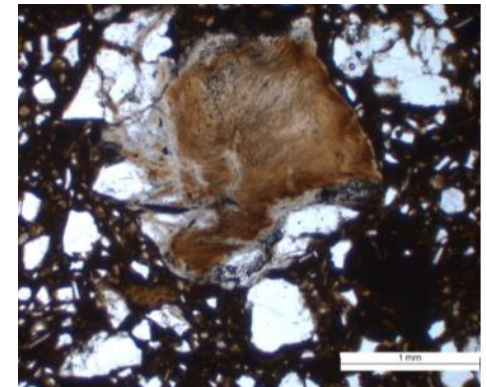
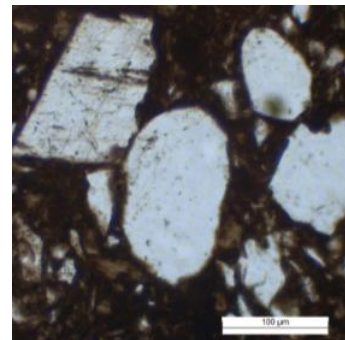
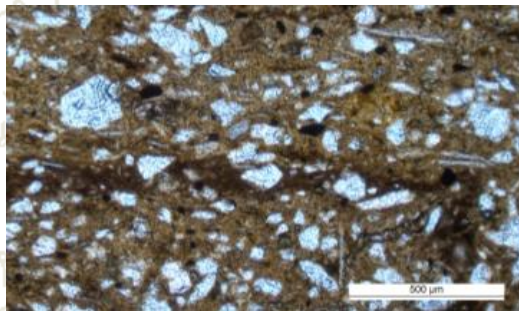
# Resultados

- Objetivou avaliar a composição da pasta cerâmica, por meio das seguintes análises:
  - Distribuição granulométrica,
  - Mineralogia de minerais granulares presentes,
  - Ocorrência de tempero,
  - Técnica de manufatura do artefato,
  - Possível conexão com as fontes de argila no entorno.

# Microscopia petrográfica

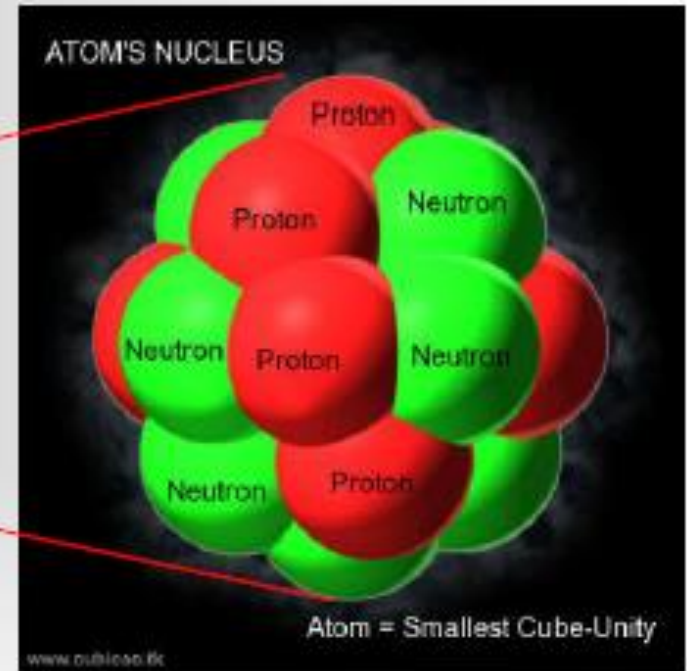
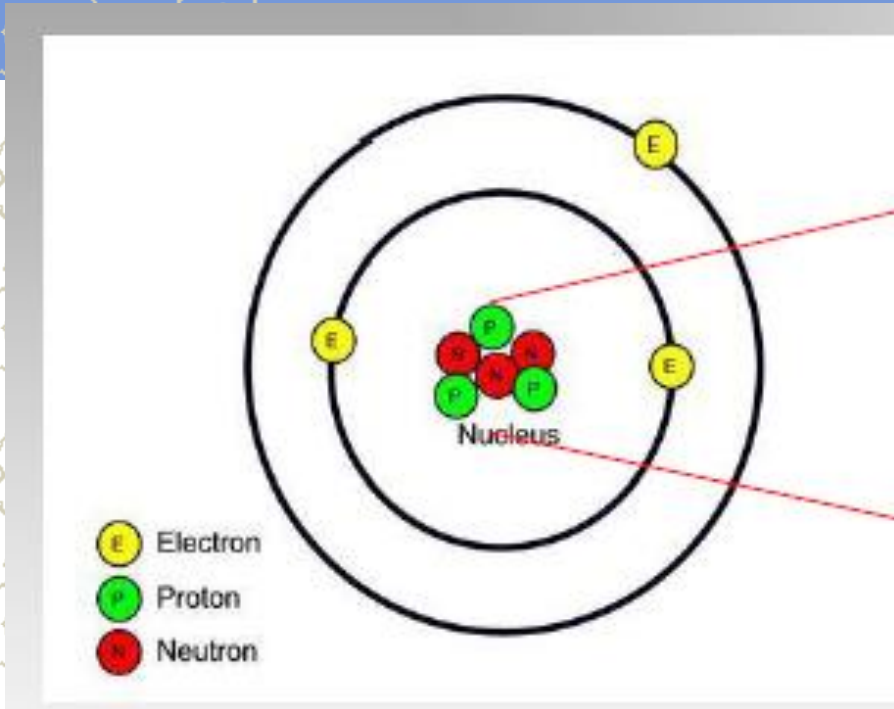


Compactação diferencial da pasta no entorno do quartzo devido a produção da cerâmica (emprego de roletes) .



Presença de quartzo, mica verde, Líticos Opacos Oxidados  
Comprovação de uso de antiplásticos (temperos) como material  
granulado, material orgânico calcinado, grãos de quartzo triturados.

# Do átomo para o núcleo



**Os processos nucleares estão presentes em nossa vida todos os momentos. Nestes processos são geradas radiações devido a processos de modificações dos prótons e nêutrons, por emissão de partículas ou por de-excitação nuclear**