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Study of historical pigments by vibrational and electronic spectroscopy

Sylvie Blanc

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28-29 March 2012 Bilbao (Spain)

Study of historical pigments by vibrational and electronic spectroscopy



Sylvie Blanc



Design of hybrid pigments

- ◆ to understand the stability of coloured historical materials
 - using simple model
 - analysing physical deterioration
 - studying chemical modification
- ◆ to describe and produce new materials
 - in archaeology
 - in art
 - optical applications
- ◆ to use non destructive methods
 - UV-Visible absorbance, reflectance, fluorescence properties
 - IR and Raman spectroscopy

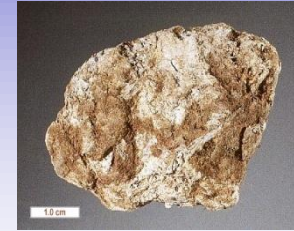
Maya blue analogues

Avignon yellow model lakes

Maya Blue

◆ ancient synthetic hybrid material

- indigo from *Indigofera* leaves
- a clay (palygorskite, sepiolite)
- heating



◆ extensively used in Mesoamerica (300-1500 AD)



⇒ exceptional stability : acid-resistant (Gettens test)
no biodegradation
stable up to ~300°C

R.J. Gettens. Am. Antiq. 1962, 27, 557

Why such a chromostability?

◆ Matrix

- indigo on the surface of palygorskite clay

Van Olphen H. Science 1966, 154, 645

- indigo in the clay channels

Chiari, G. et al. Eur. J. Mineral. 2003, 15, 21

- occlusion of the channel entrances by indigo

C. Minkowski, G. Calzaferri, Angew. Chem. 2005, 117, 5459

◆ Chromophore

- indigo forms hydrogen bonds with host silanol

B. Hubbard et al. Clays and Clay minerals. 2003, 51, 318.

- complexation of indigo with Al of the matrix

Manciu, F.S. et al. J. Raman Spectrosc. 2007, 38, 1193

- presence of dehydro-indigo

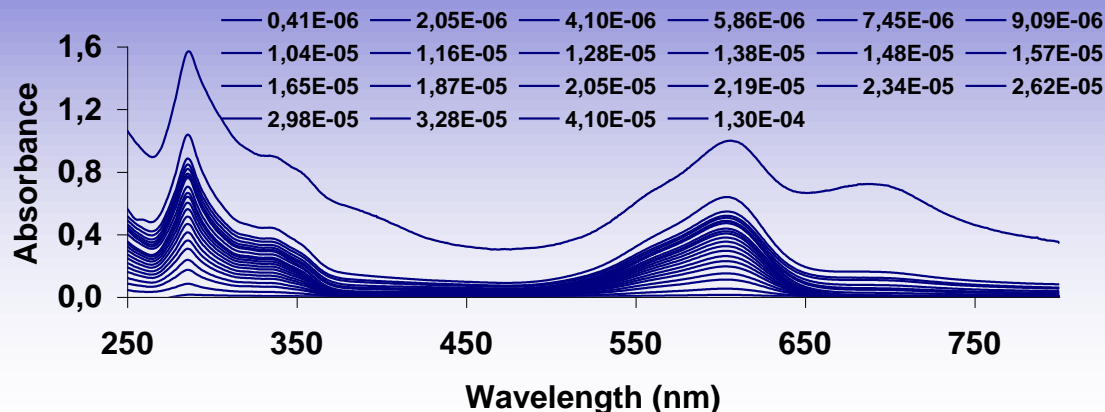
Domenech, A. et al. J. Phys. Chem. B 2006, 110, 6027

⇒ difficulty to solve the structure

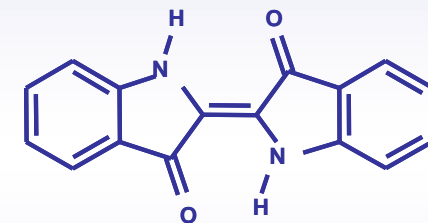
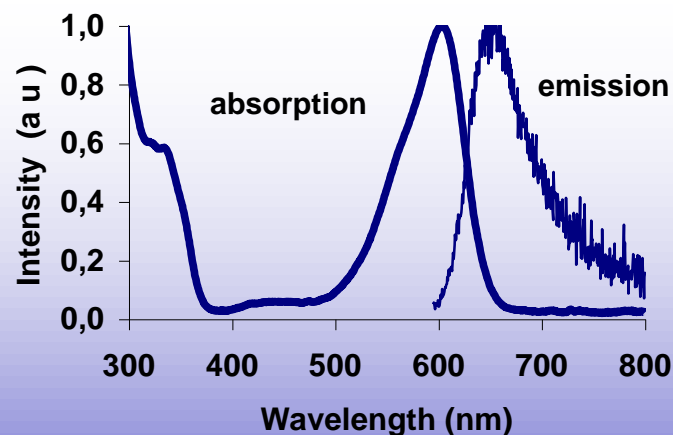
of these archaeological composite materials

Indigo visible spectroscopy in CHCl_3

◆ Absorption versus concentration



◆ Fluorescence



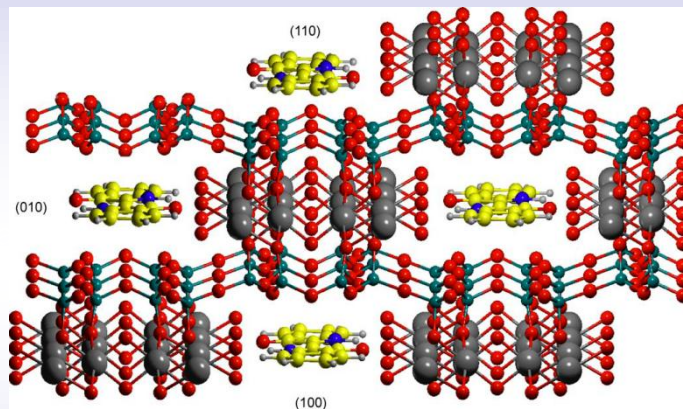
⇒ equilibrium between monomeric and dimeric species

⇒ emission fluorescence of the monomeric species

Choice of the matrix

◆ palygorskyte

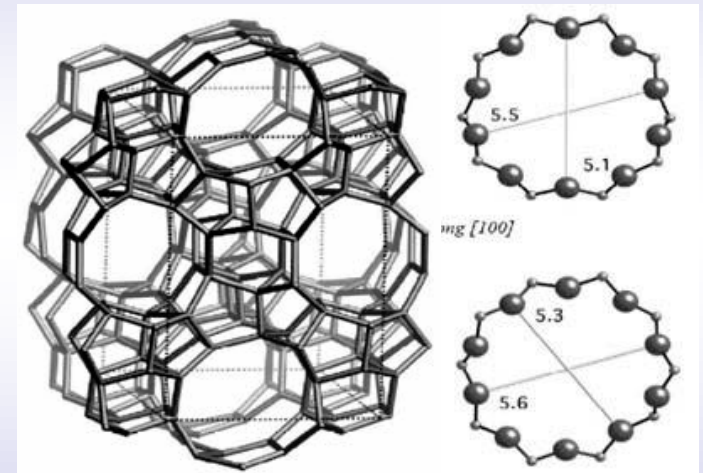
- fibrous solid



Chiari, G., Giustetto, R., Druzik, J., Doehne, E., Ricciardi, G. 2008
Applied Physics A: Materials Science and Processing 90 , 3-7.

◆ ZSM5

- Linear and zick-zack channels



⇒ resistant pigment obtained for zeolites

which pore size matches the width of indigo molecule

Synthesis of Maya blue analogs

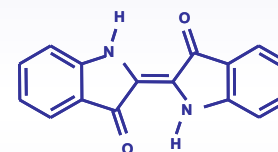
Two steps :

◆ **co-grinding (to mimic the archeological processes)**

• inorganic matrix : MFI zeolites

• organic chromophore : indigo

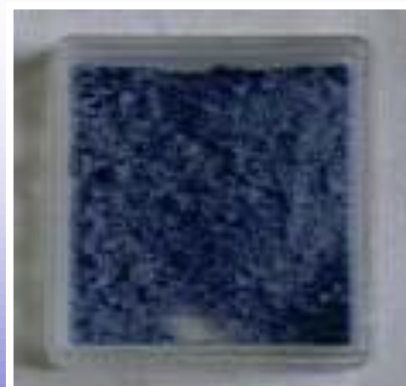
1 to 10% wt



◆ **heating up**

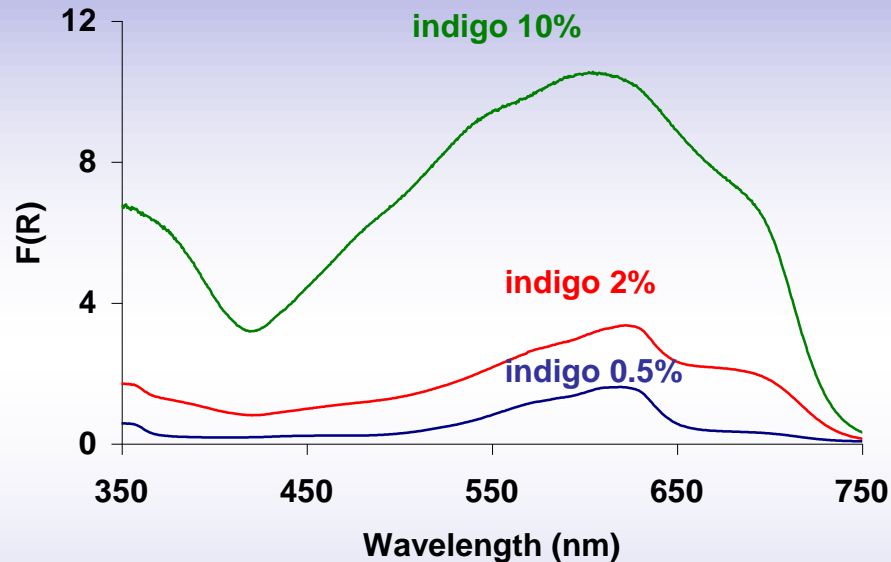
• 100-300°C

• from 2h to 15h



Maya blue analogs : species versus indigo concentration

◆ UV Visible Relectance



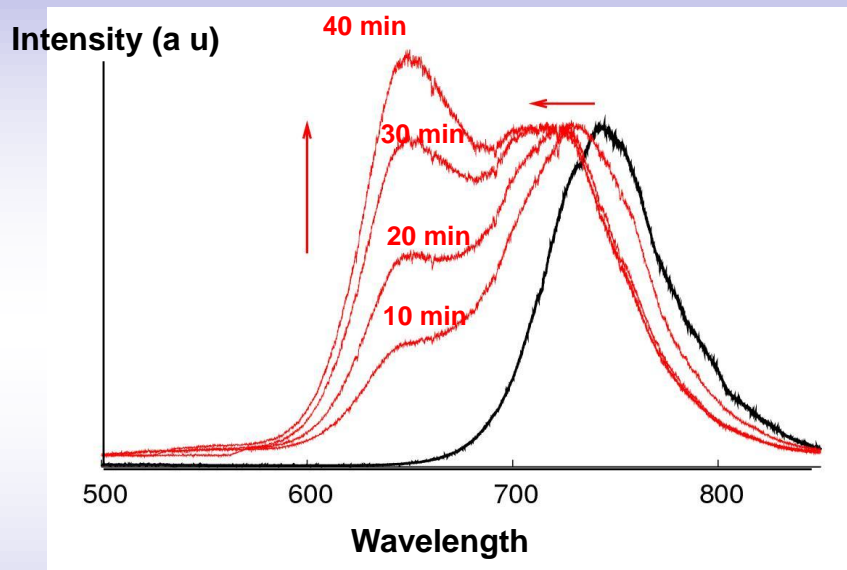
ZSM5 mixture heated in air at 200° during 5 h

⇒ **increasing intensity**

⇒ **presence of two species**

Maya blue and analogs : species versus heating time

◆ in situ fluorescence emission



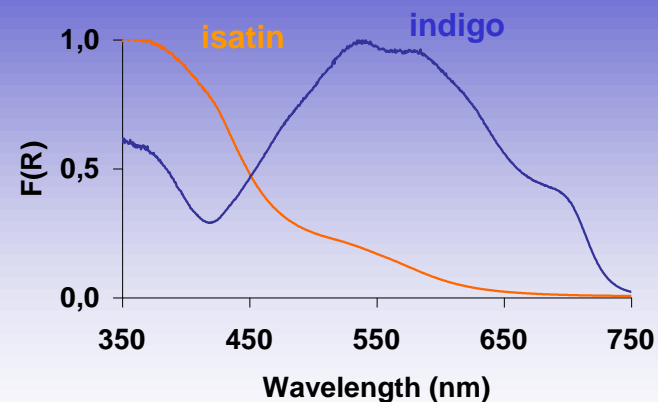
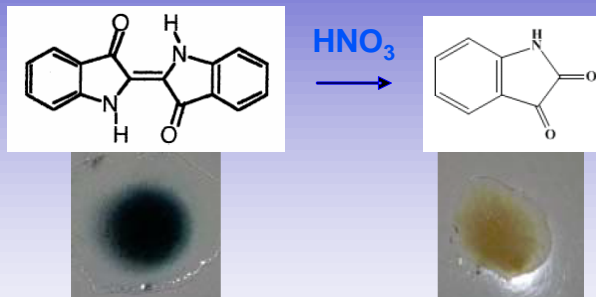
2% wt indigo ZSM5 mixture heated in air at 200°

⇒ **Mixing of dimeric and monomeric form of indigo**

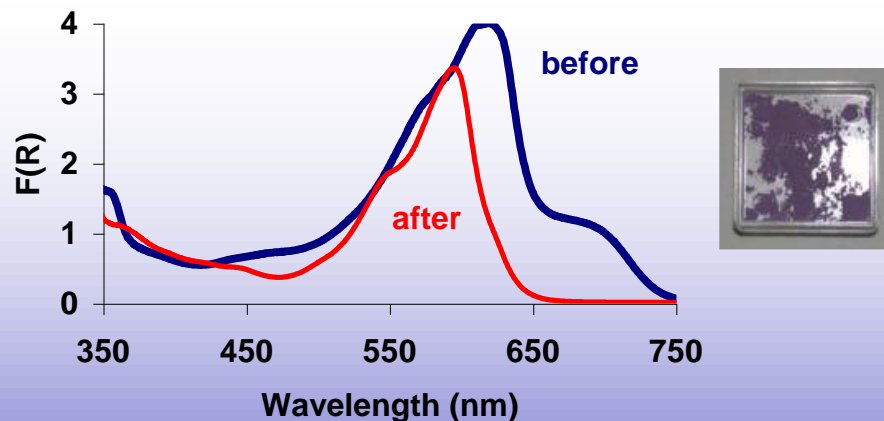
⇒ **Colour modulation**

Maya blue analogs : acid attack

◆ indigo



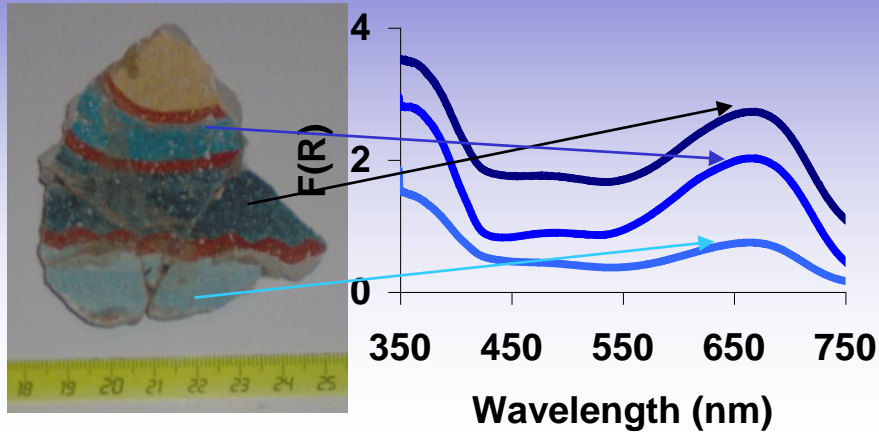
◆ ZSM5 2% indigo



⇒ The colour still persists in pigment analogs under acidic conditions

Maya Blue components

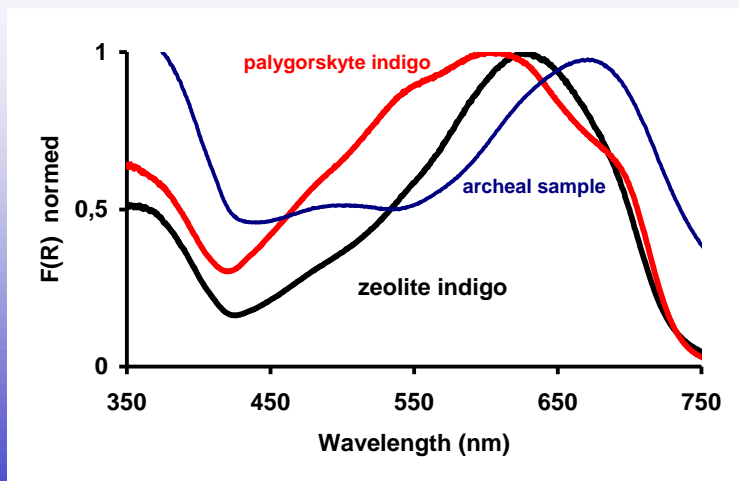
◆ Archeal sample



⇒ Indigo dilution

frescoes of Cacaxtla Coll. Louvres

◆ Colour analogy



⇒ analogs similar archeal material for low concentration of indigo

Yellow of Avignon (Stil-de-grain)

◆ Characteristics

- Yellow dyes extracted from fruits of *Rhamnus* species
- Tinctorial properties known since the Antiquity
- Employed in artistic paintings as yellow lakes
- Production in the area of Avignon (commercial place)



Livre des Jeux of Alphonse le Sage
1282 Escorial's Library

◆ History

- Lateran Council of 1215
discrimination of the Jews using yellow dye
(until the 18th century)

Preparation of yellow lakes

◆ Marcucci's « recipe »

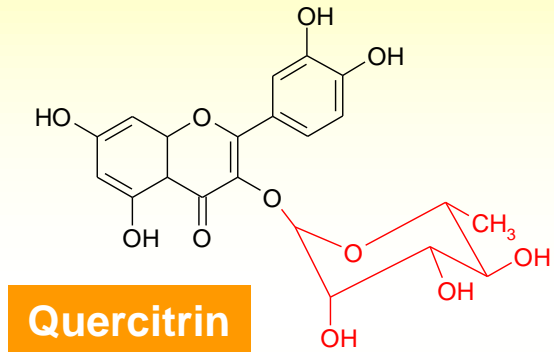
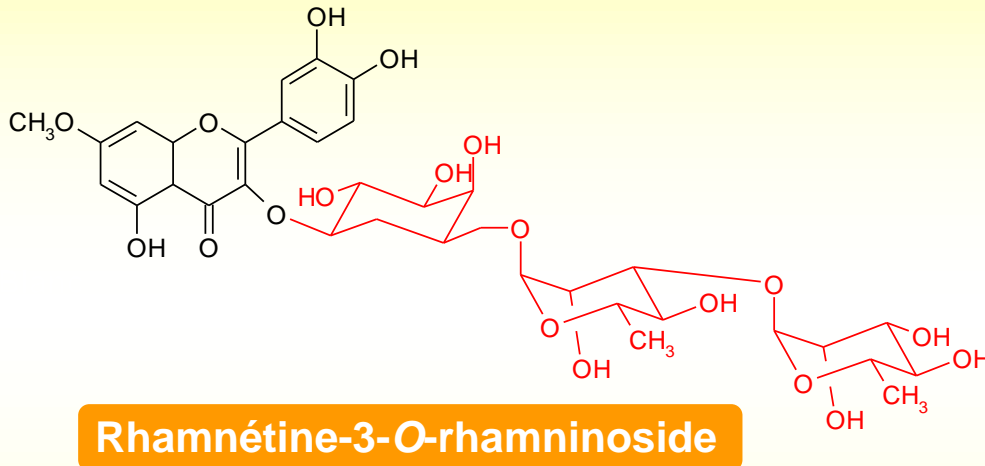
- Powdering of dried immature *Rhamnus* berries
- Maceration under agitation during 24-48 hours
- Filtration to remove the residues
- Addition of alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$)
- Precipitation of the mixture with an alcalinic carbonate



Structure, composition?

Yellow dyes of *Rhamnus catharticus*

◆ Separation and identification by HPLC-PDA

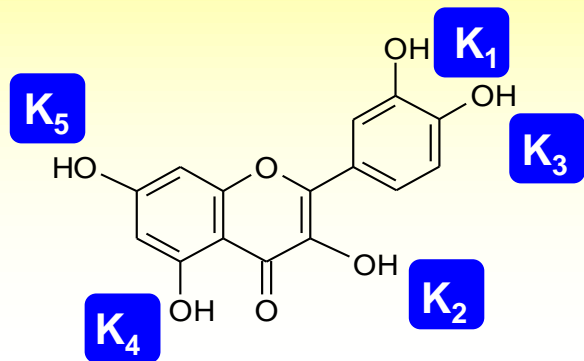


⇒ quercetin derivatives

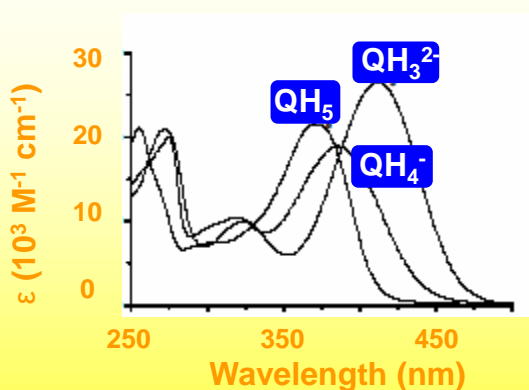
Quercetin in solution

◆ Acid-base properties

➤ Several protonation sites

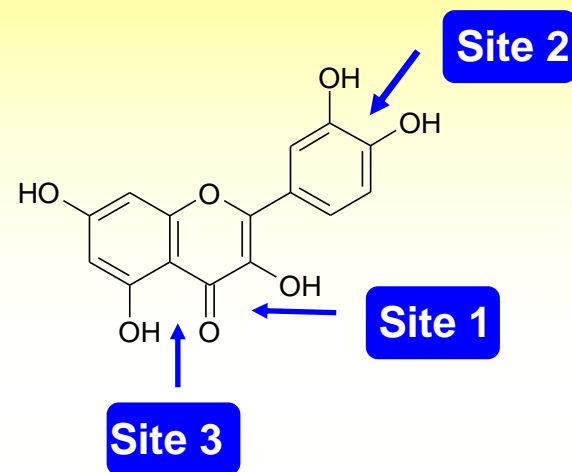


➤ Absorption spectrum versus pH



◆ Al(III) complexation

➤ Several coordination sites



➤ Several complexes

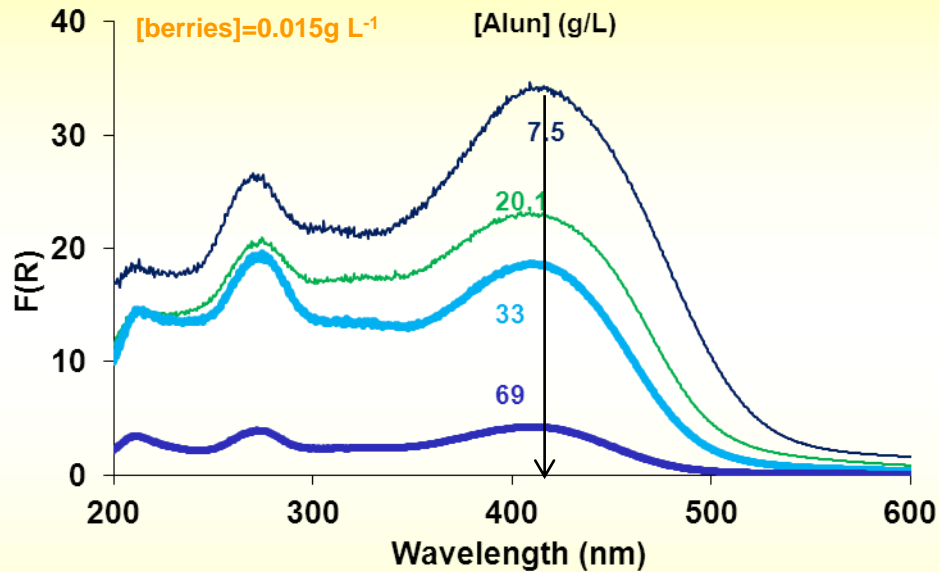
1 cation : AlQ , AlQ_2 , AlQ_3 ,
2 cations : Al_2Q , Al_2Q_3

Solid state properties?

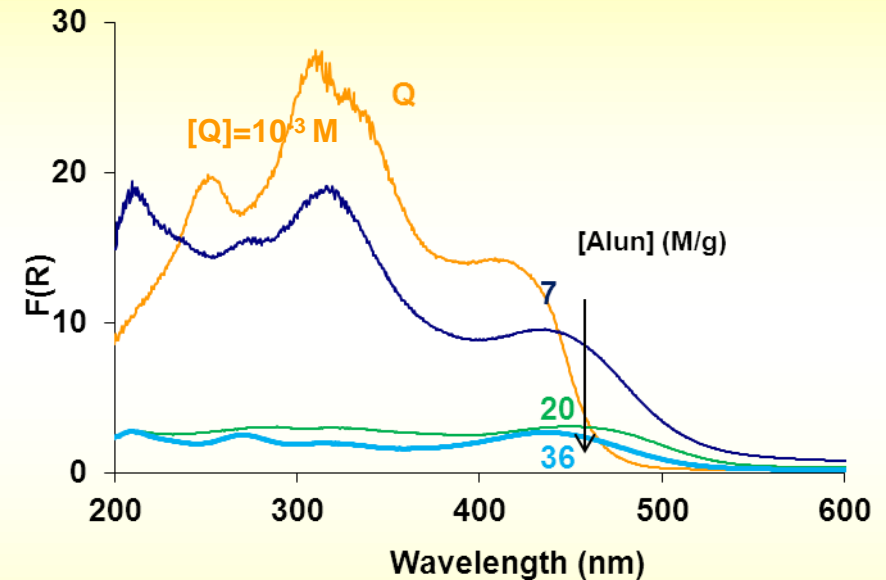
Yellow lake versus alum concentration

dye in solution + alum + carbonate

◆ Natural lake



◆ Quercetine lake

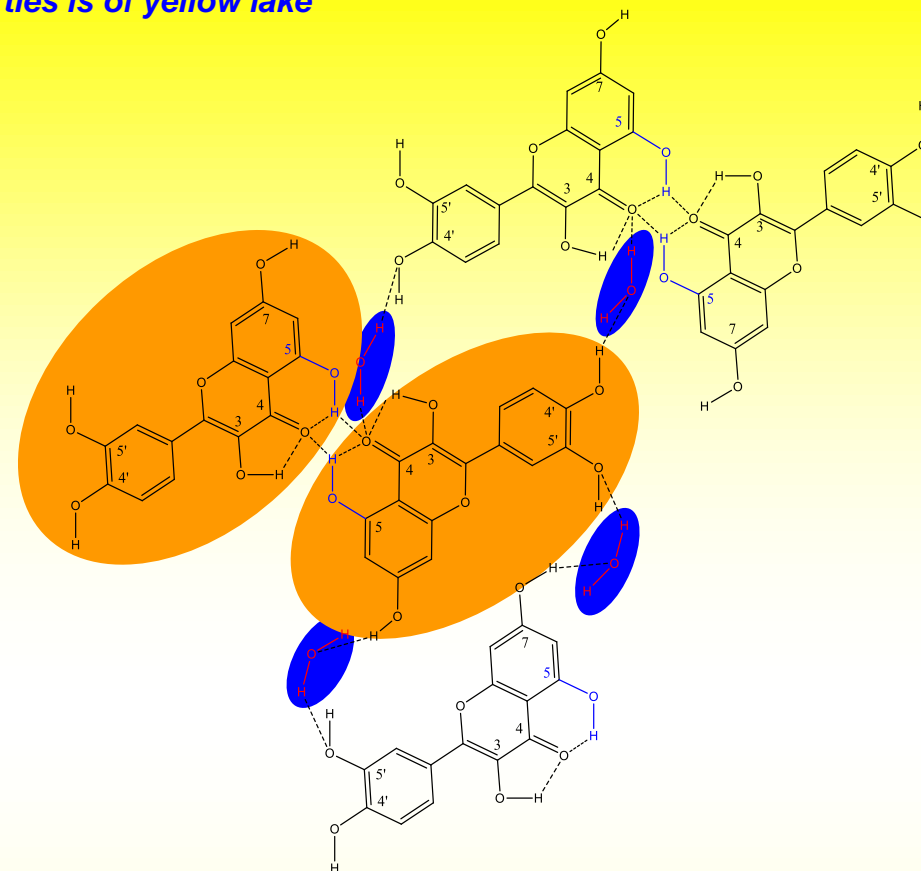


⇒ formation of an inorganic matrix of amorphous aluminium hydroxide including the organic dyes

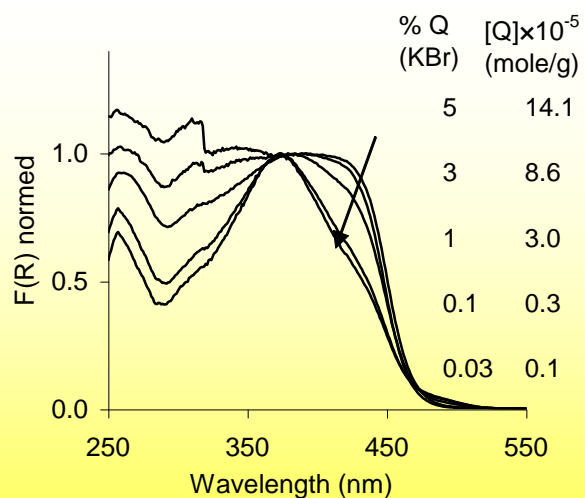
Quercetin powder

◆ Structure

- Dimer
- Dihydrate



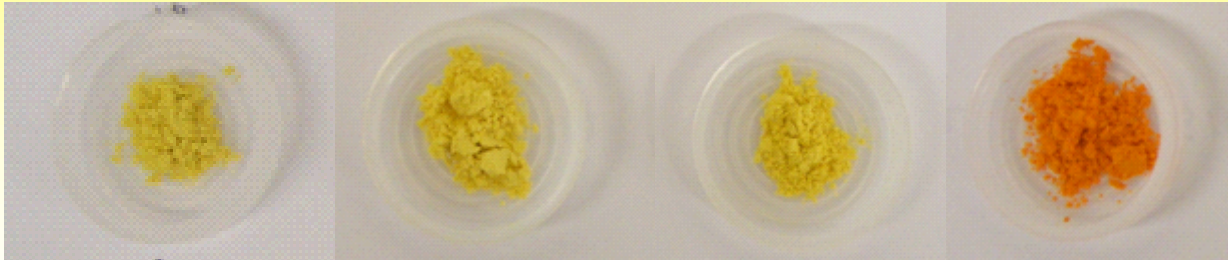
◆ DRUV



Monomer ↔ **dimer**

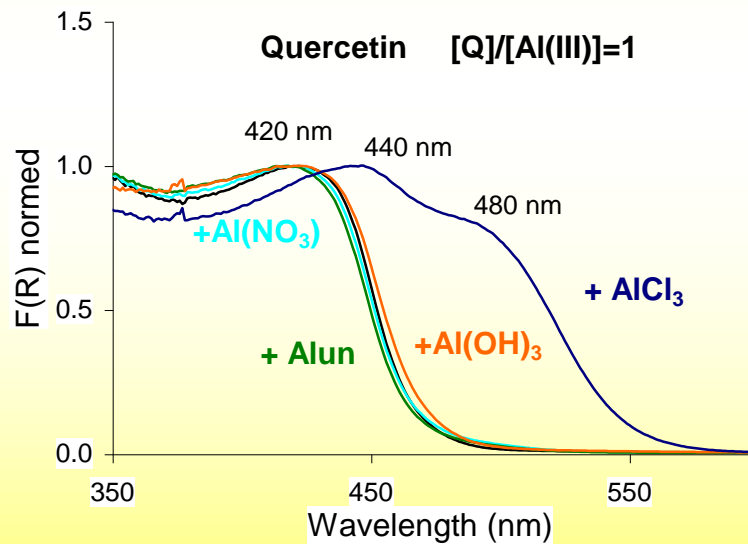
Solid state complexation of quercetin with Al(III)

quercetin + alun + $\text{Al}(\text{NO}_3)_3$ + AlCl_3



◆ Cation

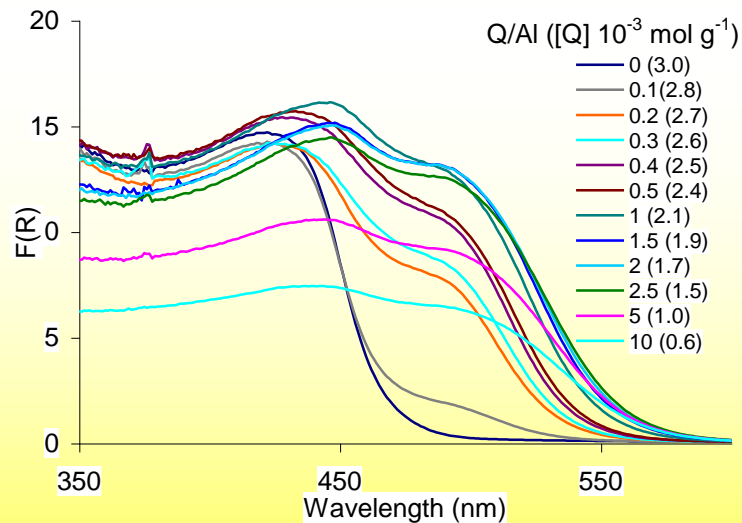
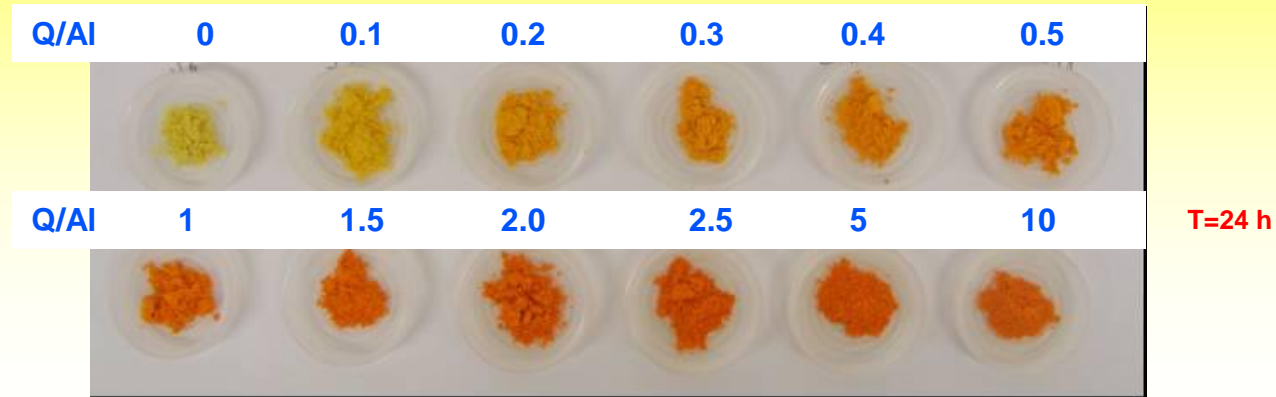
◆ DRUV



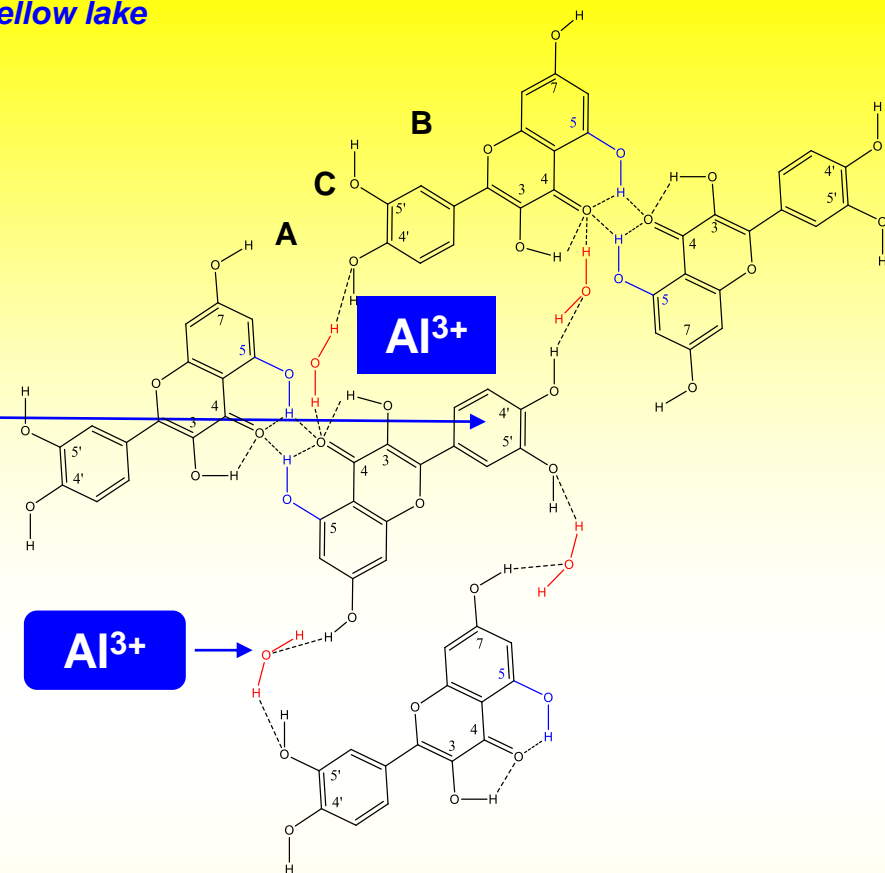
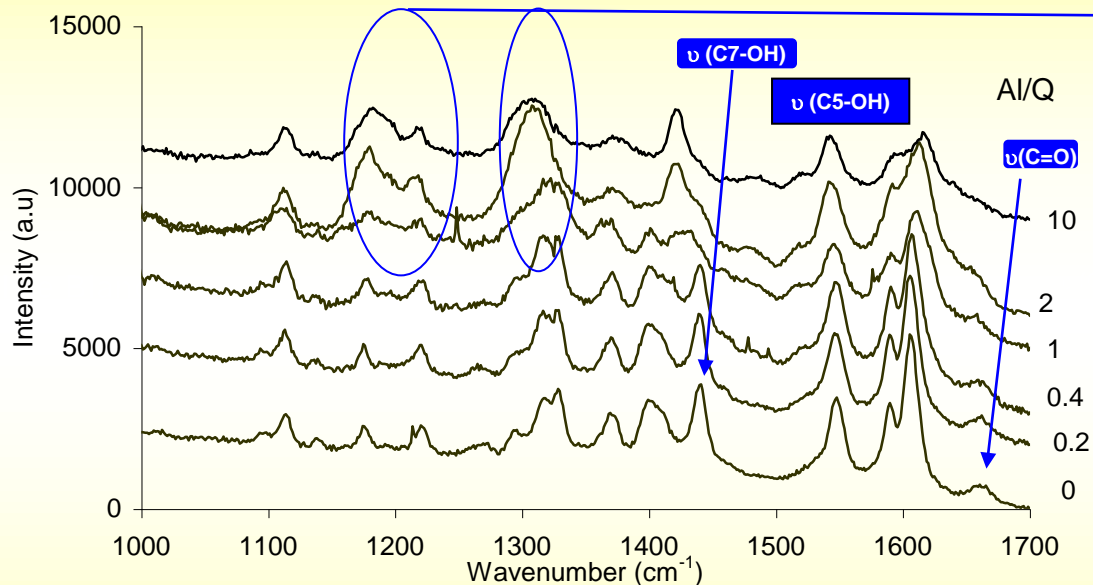
⇒ Complexation only with AlCl_3

Solid state Quercetin AlCl_3 complex

◆ Al(III) concentration



⇒ Absorption band characteristic of complexation

Solid state AlCl_3 complex : Raman

$\text{Al}^{3+} \rightleftharpoons$ water molecules

phenol coordination

Solid state AlCl_3 complex and quercetin lake

◆ Classical quercetin Lake :

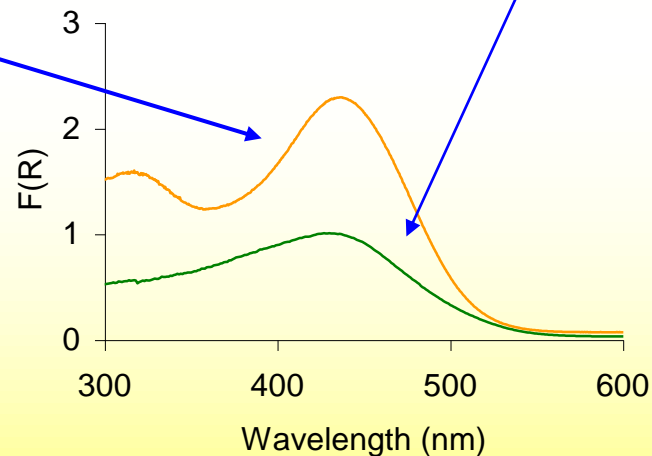
precipitate obtained by mixing
quercetin +alun+carbonate in solution

◆ Solid state quercetin lake :

$(\text{Q} + \text{AlCl}_3) + \text{Al}(\text{OH})_3$

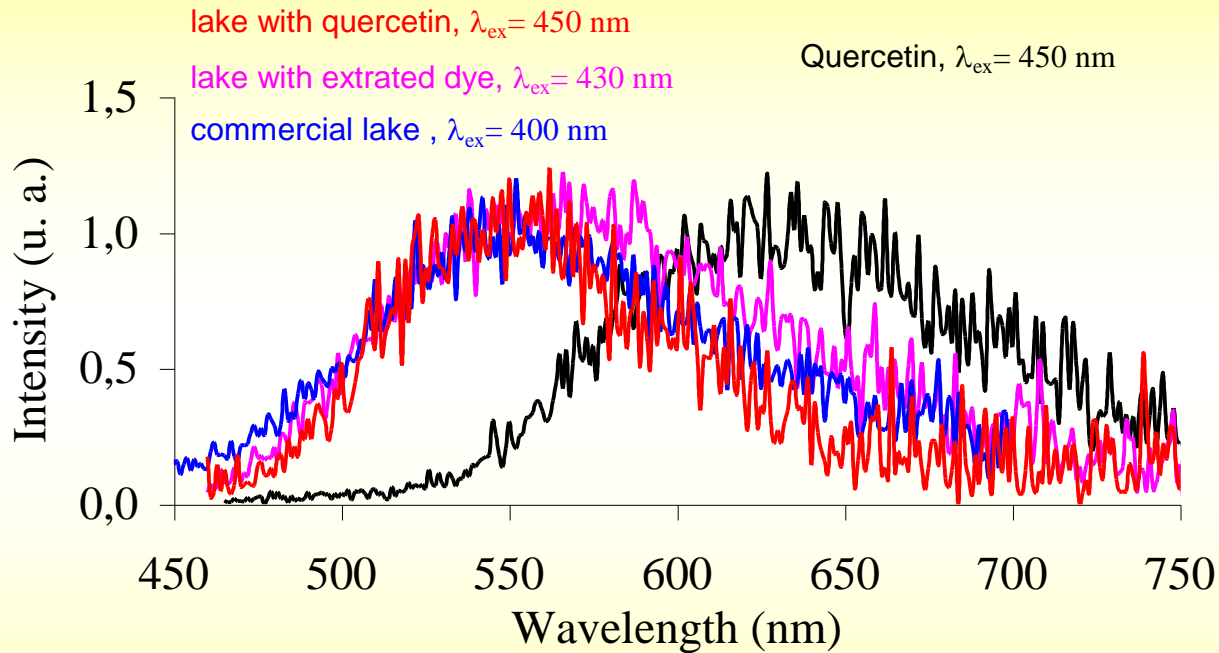
$[\text{Q}] = 10^{-3} \text{ M}$; $[\text{Alun}] = 30 \text{ g L}^{-1}$
Immediate precipitation at pH = 7 (Na_2CO_3)

$[\text{Q}] = [\text{AlCl}_3] = 10^{-4} \text{ M}$



Similar UV-Visible reflectance spectrum

Yellow lake fluorescence



⇒ **Al Complex complex emission**

Conclusion

- ◆ Identification of the yellow dyes of *Rhamnus catharticus*
 - Quercetin as chromophore model for Avignon Lake
- ◆ Quercetin powder
 - monomer and dimer observed by DRIFT and DRUV
- ◆ Solid state complexation of quercetin with AlCl_3
 - observed by DRUV and Raman
 - reaction with water molecules showed by Raman
- ◆ Quercetin lake
 - Solid state complexes similar reflectance spectrum as classical quercetin lake
 - Fluorescence properties

Perspect

From macroscopic to molecule scale

◆ fluorescence microscopy

Sylvie Blanc

◆ molecular dynamic simulation

COLHYBRI

Sorption process of dye molecules in organic-inorganic complexes : a route from Maya Blue to novel hybrid colorants

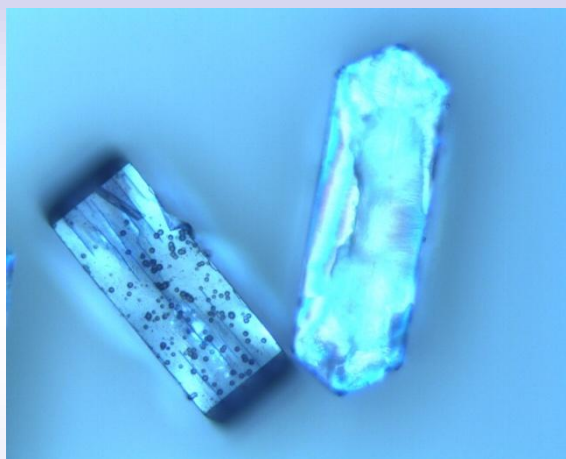
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