Non destructive methods to identify the components and the techniques of works of art

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Overview

• Pigments and dyes identification
  - Upper layer: reflectance spectra and databases
  - Under layer: OCT, RTE?
• Varnishes
  - Topography: confocal microscopy, OCT
  - Identification: UV fluorescence
  - Virtual removing
• Artistic techniques
  - Gold techniques (goniophotometry)
  - Glazes (colorimetry, RTE)
Pigments and dyes identifications

Gonio-spectro-photo-colorimeter in back-scattering configuration
Pigments and dyes identifications

Carolingien manuscript of St Amand les Eaux’ scriptorium, IXth c.

Gonio-spectro-photo-colorimeter in back-scattering configuration
Pigments and dyes identifications

Olivier Mosset, Gone West, 1987
FRAC Dijon
Yellow laq Maimeri

G.Dupuis, M.Elias, L.Simonot, Pigment identification by fiber-optics diffuse reflectance spectroscopy”, Appl. Spectrosc. 56 n°10 (2002)1329-1336
Pigments and dyes identifications

Etienne Chevalier’s « livre d’heures » Jean Fouquet ≈1450
Chantilly Museum

R(%) vs λ(nm)

Blue areas: lapis-lazuli

Surface state ⇒ translation \( R_{surf} \)

St Apolline’s martyrdom

St Nicolas’ consecration

St Catherine’s martyrdom

St Hilaire’s consecration
Pigments and dyes identifications

Numerous spectra

Multi spectral camera (Lumiere et Technology SAS)

⇒ 100,000,000 reflectance spectra
Pigments and dyes identifications

formulation software Colibri (Ciba, Minolta) + colour chart pigment mixture recognition

Lapis Lazuli + White lead

Red ochre + Umber

Lead tin yellow + White lead

Umber

Ochre + Verdigris

Yellow ochre + Umber

Multispectral camera (Lumiere et Technology SAS)
Pigments and dyes identifications
Composition of Mona Lisa’s sfumato

Unvarnished spectra
Pigments and dyes identifications
Composition of Mona Lisa’s sfumato

Spectra → colour L*a*b* space
Pigments and dyes identifications

Composition of Mona Lisa’s sfumato

Modelling using RTE solved by AFM

M. Elias, P. Cotte “Multispectral camera and radiative transfer equation used to depict Leonardo's sfumato in Mona Lisa” Applied Optics, Vol. 47, n°12, pp. 2146-2154
Pigments and dyes identifications

Identification in the upper layer
- Goniospectrophotocolorimeter (1 spectrum)
- Multispectral camera (100,000,000 spectra)

Identification in the under layer
- Modelling using the radiative transfer equation (systemization in progress)
- OCT in the visible range (in progress)
Varnishes

Topography: confocal microscopy

µsurf microscope – Nanofocus
European project FingArtPrint
Varnishes

Topography: cross section

Paint + mastic in turpentine

Confocal microscopy

OCT

Same accuracy $\approx 1.5 \, \mu m$
Varnishes

Topography: cross section profile

Paint + mastic in turpentine

⇒ Thickness varnish = 16 × 1.5 = 24 µm
Varnishes

Topography: cross section profiles

Metal + aged mastic in linseed oil  
Metal + aged mastic in turpentine  
Metal + fresh mastic in turpentine

⇒ Thickness of the varnish measurable ∀ binder ∀ ageing
Varnishes

Topography: Interfaces imaging

Interface air/varnish

Interface varnish /paint
Varnishes

**Topography**: Interface profiles

- **Interface air/varnish**
  - r.m.s. roughness $h = 2.0 \ \mu m$
  - correlation length $l = 16.6 \ \mu m$
  - $h/l = 0.1$

- **Interface varnish /paint**
  - r.m.s. roughness $h = 2.0 \ \mu m$
  - correlation length $l = 16.6 \ \mu m$
  - $h/l = 0.1$

*R. De La Rie, J. Delanay, E. Charron, Leveling of varnishes over rough substrates, Opt Com 266 (2006) 586-591*
Varnishes

**Identification**: UV fluorescence emission spectra

Spectrofluorimeter Jobin - Yvon

Gonio-spectrometer in back-scattering configuration
- powerful UV-LED / laser + frequency doubler
  - silica optical fiber
**Varnishes**

**Identification**: UV fluorescence emission spectra

**Influence of the UV excitation**
- $\lambda_{\text{exc}} = 320\text{nm}$
- $\lambda_{\text{exc}} = 400\text{nm}$
- mastic

**Influence of the recipe**
- mastic + linseed oil
- mastic + turpentine

**Influence of the resin**
- $\lambda_{\text{exc}} = 360\text{nm}$
- dammar
- mastic

**Influence of the ageing**
- fresh mastic
- aged mastic
- old mastic (100 years)
Varnishes

**Identification:** UV fluorescence emission spectra

**Protocol:** 1 database for 1 $\lambda_{\text{exc}}$

unknown spectrum $\leftrightarrow$ spectral databases

**Criteria:** $\lambda_{\text{max}}$ and/or $\Delta \lambda$
Varnishes

**Identification:** UV fluorescence emission spectra

La Madone Hesselin- Simon Vouet, 1640, Le Louvre

Varnish = mixed aged mastic

Varnishes

Virtual removing

Experimental method:

Colophony aged varnish
Mastic aged varnish

Colour chart

Ratio b/a applied for each λ on the recorded spectra
Varnishes

Virtual removing

Analytical method:

- surface leveling
  \[ \Rightarrow \text{downward translation } A \]
  +
  - absorption: \[ I = I_o \exp(-\alpha h) \]
  with \[ \ln \alpha = -0.016\lambda + 17.2 \]
  and \[ h = \text{approximative varnish thickness} \]

M. Elias, L. Simonot, M. Thoury, JM Frigerio, Bi-directional reflectance of a varnished painting
Part 2: Influence of the refractive indices, surface state and absorption – Experiments and
Results for the Joconda

Today

After a virtual half removing of the varnish

After a virtual varnish removing
Artistic techniques
Gold techniques: goniophotometry

- Gold paint
- oléo-resinous mixtion
- « bol » aqueous medium
Artistic techniques

Gold technique: Issenheim’s altarpiece - Grünewald (1510 – 1516)
Unterlinden Museum- Colmar

Angels’s concert

The column of the Angel’s concert is made with gold on mixtion

Artistic techniques

Glaze and Pigment mixture

reflectance spectra → colour Lab

\[ C^* = \sqrt{(a^2+b^2)} \]

Artistic techniques

Glaze and Pigment mixture

Issenheim’s altarpiece - Grünewald (1510 – 1516)
Unterlinden Museum- Colmar

Grünewald used a glaze technique in Gabriel’s drape
Artistic techniques

Glaze and Pigment mixture

Léonardo used a glaze technique around 1505

Is the Lady with Ermine (Cracocia) made of a glaze?
You are invited in the European City of Science
Grand Palais – Paris – the 14-16th of November 2008

« Le musée des œuvres revisitées »

Thank for your attention