Photodetectors at « Le Louvre »
X-ray, γ-ray and visible spectrometries
applied to Art and Archaeology issues

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Outline

• Presentation of the C2RMF
• Examination of artifacts
  • Visible light, IR reflectography, UV fluorescence XR imaging
  • examples of application to examination of paintings and sculptures
• Characterisation of materials
  • Introduction to accelerator-based methods
  • Example of detection of fakes using chemical composition
  • Example of materials identification and determination of provenance
• Specific problems
  • Improvement of the sensitivity to trace elements
  • Chemical environment with Hi-Res X-ray spectrometry
  • Portable detection systems for on-the-field analysis

Conclusions and prospects
Presentation of the Center for research and restoration of the museums of France (C2RMF)

Belongs to the French Ministry of Culture
Created in 1999 by the merging of the laboratory and restoration centre

Laboratory

- Founded in 1931 by 2 Argentinean physicians
- Located in Paris under the Carrousel gardens of the Louvre
- Staff ~70 : Culture (curators, engineers), CNRS, CEA
- Associated with CNRS since 1996 – UMR 171
Location of the C2RMF
Missions of the C2RMF

- Diagnosis, short studies on art and archaeology works
  - acquisition (authentication)
  - restoration
  - exhibition

- Long-term research
  - archaeometry: studies of ancient technologies and provenance
  - conservation science: understanding the artists techniques
  - preventive conservation: investigation of alteration process

- Publishing and teaching
Main tools for examination and characterisation of cultural heritage

- **Examination of artifacts**
  - Visible light, IR reflectography, UV fluorescence
  - X-ray imaging, betagraphy, emissiography
  - Scanning electron microscope (SEM) imaging

- **Characterisation of materials**
  - Structural analysis: XRD, FT-IR, Raman
  - Inorganic chemical composition: IBA, XRF, SEM-EDX
  - Organic composition: Chromatography, GC-MS

- **Dating**
  - Thermoluminescence
  - $^{14}$C using accelerator-based mass spectrometry
Examination of works of art

Paintings and sculptures
Photography with direct and grazing light: evidence of the Van Gogh’s technique in « Mademoiselle Gachet au jardin »
Venus Genitrix
1st-2nd AD
visible light
ultraviolet
Venus Genitrix (detail)
restored hand made in a different marble
Principle of infrared reflectography: access to the charcoal underdrawing.

Mid-range infrared (1.8-2.5 µm)
Examination by infrared reflectography
Radiography studio for paintings
Radiography of the «Gobeur d’oursins» of Picasso (1946): painted on top of a portrait of Gal Vanderberg

Radiography
Examination of a Spanish painting from the XVIth century

direct light

grazing light
Spanish painting:
UV fluorescence reveals restorations
visible light  ultraviolet
Spanish painting:
X-rays reveals a second character: part of a wider composition

Infrared

Radiography
Analysis of material using non-destructive techniques: the case of accelerator-based methods
Fundamentals of PIXE et PIGE methods

( Particle Induced X-ray Emission et Particle Induced γ-ray Emission )

- Beryllium: $^{9}\text{Be}(p,\gamma)^{6}\text{Li} \ 3562 \text{ keV}$
- Lithium: $^{7}\text{Li}(p,p'\gamma)^{7}\text{Li} \ 477 \text{ keV}$
- Fluorine: $^{19}\text{F}(p,p'\gamma)^{19}\text{F} \ 197 \text{ keV}$

- 3-MeV protons
- Expelled electron
- Target atoms
- Particle Induced X-ray Emission et Particle Induced γ-ray Emission
- Accelerator
- HPGe detector
- Si(Li) detector
Accelerateur Grand Louvre pour l’Analyse Elémentaire

2-MV tandem accelerator « AGLAE »

Control and data acquisition room
PIXE external beam setup and experimental conditions

Proton energy : 3 MeV
Beam intensity : 2 nA
integrated dose : 0,25 µC -> no damage
beam diameter on the target : 20 µm
beam exit foil : 0.1 µm silicon nitride

<table>
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<th>« high energy »</th>
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<tbody>
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<td>L -detector</td>
<td>H - detector</td>
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<tr>
<td>entrance window</td>
<td>0.25 µm boron</td>
<td>6 µm Be</td>
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<tr>
<td>absorber</td>
<td>1 µm carbon</td>
<td>100 µm aluminum</td>
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<tr>
<td>element range</td>
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<td>trace elements</td>
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<tr>
<td></td>
<td></td>
<td>calcium-yttrium</td>
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<tr>
<td>solid angle</td>
<td>1 msr</td>
<td>100 msr</td>
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Close-up of the external beam system

Low energy X-ray detector for major elements e.g. Al, Si...

High energy X-ray detector for trace elements e.g. Cr, Ti, V, Fe, Ca...

Target: gemstone

Charged particle beam exit

Video camera

Helium flux

HPGe γ-ray detector
Main features of accelerator-based methods

Benefits

• non-destructive analysis of objects with any shape and size
• no sampling, no preparation (conductive coating etc.)
• simultaneous measurement of a wide range of elements (10 < Z < 92)
• sensitivity to trace elements (down to the μg/g level)
• 30 μm³ probed volume: selection of details
• truly quantitative methods
• elemental maps (micro and macroscopic scale)

Disadvantages

• no information about the chemical state
• no structural information (XRD, IR, Raman)
• near surface (1 – 30 μm) (problems with altered objects)
• expensive large scale facility
First application of the PIXE method:
Indirect dating of paintings

The portrait of Bernard Palissy

Painting supposedly representing B. Palissy, French scientist and artist of the Renaissance (1580-1620)

Proposed to be acquired by the French museums
First application of the PIXE method: detection of forgeries

Presence of CrPbO$_4$ green pigment only introduced after 1850

- This painting is probably a forgery
Application of the PIXE method: materials identification and provenance

Ishtar’s eyes

Statuette exhibited in the Louvre museum
Dated to the Parthian period (1st BC – 2nd AD)

Likely representing Ishtar, the famous Mesopotamian mother goddess

(Astarté or Venus)

Discovered in 1863 in the vicinity of Babylon
The statuette is placed in the external beam system
PIXE spectra recorded on one eye

The graph shows the high energy X-ray detector spectrum in blue and the low energy X-ray detector spectrum in red. The peaks at different X-ray energies correspond to the K-shell emissions of various elements, including Al K, Ti K, V K, Cr K, Fe K, and Ga K.
RUBY  Red corundum  Al$_2$O$_3$

Coulour due to trace amount of Cr

$\rho = 4.00 \text{ g.cm}^{-3}$

$n = 1.76$

$H = 9$
Map of Middle East and Asia: sources of rubies
Trace element fingerprint of rubies from Ishtar and various deposits

- **Group I**: Burma, Vietnam A
- **Group II**: Afghanistan, Sri Lanka, Vietnam B
- **Group III**: Thailand, Cambodia, Kenya, Madagascar, India

**Statuette of Ishtar**
Proof of authenticity of the statuette

Original report of Mr. P. Delaporte, French consul at Bagdad who discovered the statuette

Document written at Hillah, close to Babylon

January 21, 1863
The eyes and the navel of Ishtar are not made of red glass, nor red garnets, as previously reported, but rather proved to be fine rubies.

According to the age of the statuette, this is the most ancient rubies found in Middle-East.

Evidence of a gem route between South-East Asia and Mesopotamia during the 1st century BC.
The jewels of the first kings of France
Saint-Denis Basilica (north of Paris)
cemetery of the kings of France
since the Merovingian
paire of brooches
450-500 A.D

plaque-boucle
470-500 A.D

plaque « bull »
480-510 A.D

5-digits brooch
~500 A.D

2 square brooches
500-550 A.D

pair of brooch
500-520 A.D

2 disc brooches
« reine Aregonde »
575-600 A.D

Quatrefoil brooch
600-625 A.D
The garnets

H = 6½ - 8½
r = 3.5 - 4.3 g.cm⁻³
n = 1.78 - 1.89
Chemical composition of garnets

$$\text{A}_3^{++}\text{B}_2^{+++}\text{(SiO}_4\text{)}_3$$

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<th>end-members</th>
<th>Almandine</th>
<th>Pyrope</th>
<th>Spessartite</th>
<th>Grossular</th>
<th>Ouvarovite</th>
<th>Andradite</th>
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<td>Fe</td>
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Actually garnets are a solid solution of end members.

Example:

Rhodolite = mixing of 50% pyrope / 50% almandine.
Fe/Mg plot: three groups of garnets

- Pyropes
- Rhodolites
- Almandins
Ca/Mg plot: 2 types of almandines

- Almandines:
  - Type I
  - Type II

- Pyropes:
  - Types IV & V

- Rhodolites:
  - Type III

- Others:
  - Quatrefoil
  - 5 fingers brooch

[Graph showing CaO vs. MgO plot with various markers representing different types of gemstones]
Yttrium content confirms 2 sources of almandines
Scattered content in yttrium: macroscopic zoning
Comparison with published data on garnets:
Quast & Schlüsser 2000 (SEM-EDX)
Results

- The garnets set on the Merovingian jewels were extracted from **India** and **Sri Lanka**.
- Evidence of **two sources** **Indian deposits**.
- Coming from the East during the great Invasions, the first Frankish kings have kept their sources oriental of garnets.
- On the latest jewels (7th century), the type of garnets changes: pyropes from **Bohemia**.
- Surprisingly from the 5th to the 7th century AD, the Barbarians have established a gem route to Asia.
study of provenance of gold used in Merovingian jewellery

The key feature for improving the limit of detection is the Peak/Background ratio of X-ray detectors

The interesting trace element are the Platinum Group elements (Ru, Rh, Pd, Os, Ir, Pt and Sn Sb). Typical content is 100 µg/g. The related lines lie in the 20 keV-range. Pt has its lines just underneath the Au lines at 9.44 keV.
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- Improve manufacturing technology (reduce charge collection loss).
- Reduce shaping time / use digital pulse processor in order to reduce sum peaks.
Hi-res spectrometry for chemical speciation

- Chemical state (valence) accessible by means of X-ray satellite peaks resulting of bombardment with heavy particle (multiple shell ionization).
- WDS?
- μ-Calorimeter?
development of a portable XRF system for on the field analysis (museum, archaeological site…)

- Peltier-cooled Si-drift diode
- 300-µm crystal thickness: efficiency drops above 10 keV
- ageing problems
- poor peak/background ratio
Conclusion

- The photon probe, due its non-destructive character, is recognised as a valuable tool for study of art and acheological artifacts

- The study of cultural heritage will benefit from developments in photodetectors
Encouraging prospects

Good old Mona Lisa... investigated using a state of the art detector... ...and with a new generation photodetector