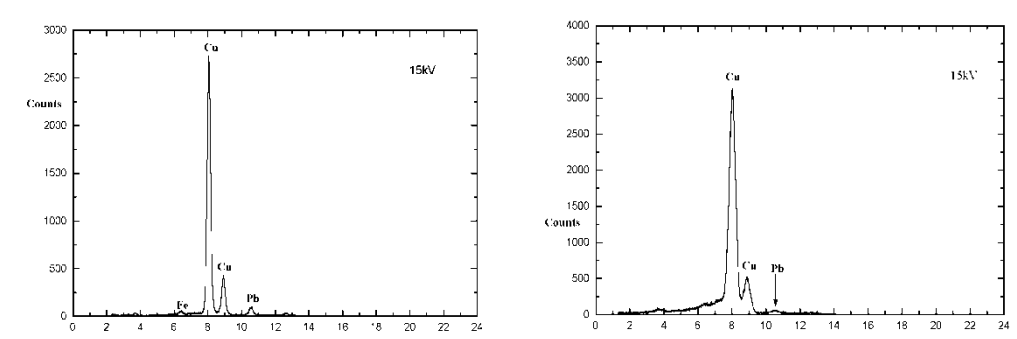


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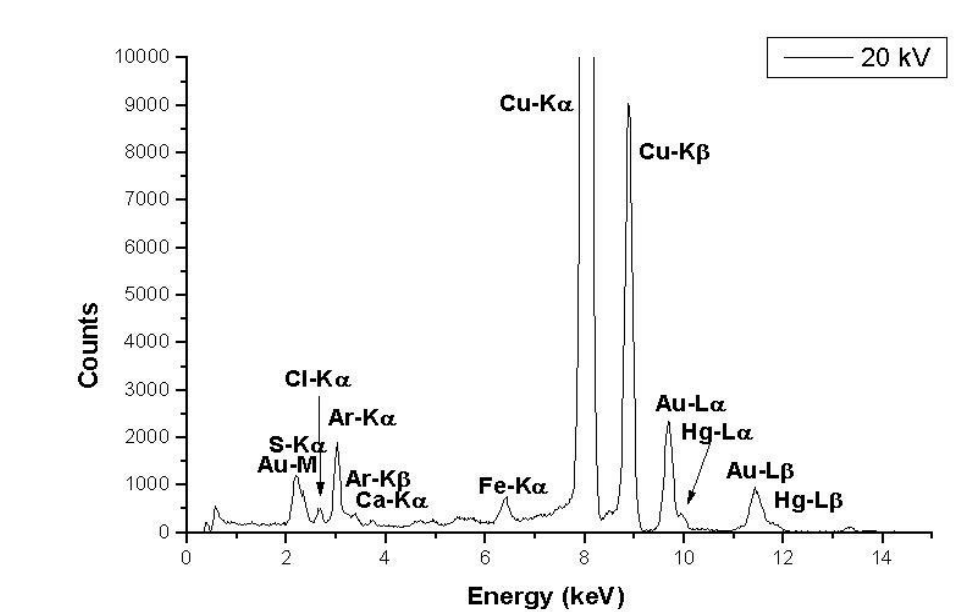
The Material Science Institute of the Valencia University (ICMUV) has been involved throughout last 25 years in the development, evaluation and analytical applications of physic-chemical techniques in the field of the Cultural Heritage analyses. The Archaeometry Unit aims to the definition, the implementation and the validation against selected case studies of experimental protocols for analysis, diagnostics, conservation and restoration of artistic objects as paintings, sculptures, metals, glasses, ... Here, we present some examples of our research in this field.



Paintings from the "Retaule de l'Altar Major" and spectra of some blue zones.

TECHNOLOGICAL INFORMATION

- The EDXRF technique can give us information about the process of making the work of art and the state of preservation, which could be important to determine its value:
- "Retaule de l'Altar Major de la Catedral de València", Hernando Llanos and Yañez de la Almedina, 1507-1510.
→ In the contract between the authors and the owners, the use of blue ultramar, $3\text{NaAlSi}_3\text{O}_8 \cdot \text{Na}_2\text{S}_3$, was accorded. This is a very expensive pigment. However, 10 points of different tonalities of blue have been analysed and none of them show sensitively the sulphur (2.3 keV) and the silicon (1.7 keV) peaks. A high quantity of copper (8.1 keV) is observed, which could indicate that azurite was mainly used.
- "Screws of the plates of the cupola of St. Isaac Church of St. Petersburg"
→ The corrosion is due to the formation of copper sulfides and chlorides. The presence of mercury indicates that the technique used to gold-plate them was the amalgam of gold and mercury with a later heating to evaporate the mercury. The same technique has been found in the "Moon Pope's Chalice".



"The Moon Pope's Chalice"

STUDY OF THE DEGREE OF ORIGINALITY OF ART WORKS

The EDXRF analysis can help to see which part of the work of art corresponds to the original author and which one is due to later interventions. Here, we present three examples.

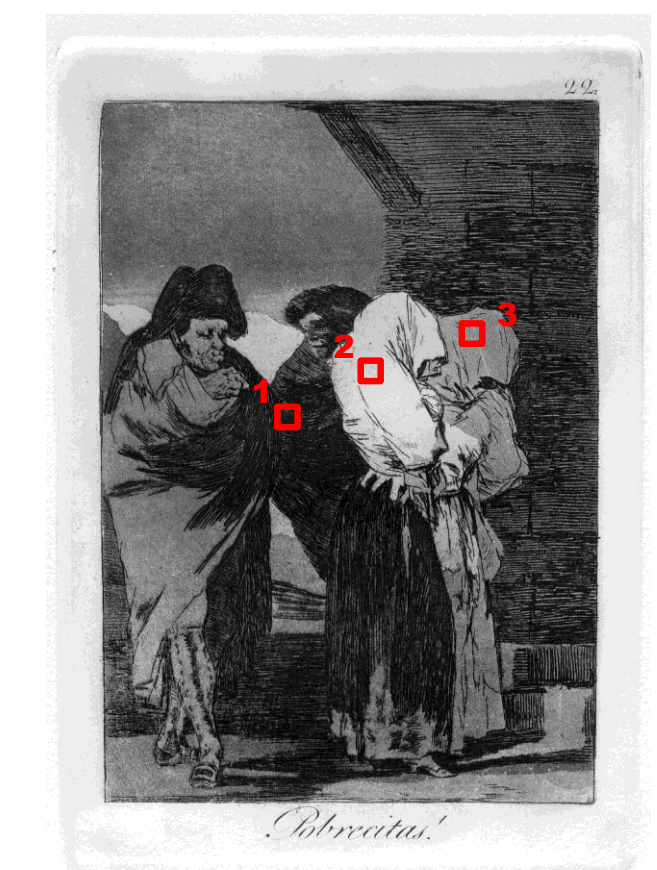


"Fondo de Lucillo Funerario Gótico de la Iglesia de San Esteban de Cuéllar" from the Museo Arqueológico Nacional, end of the XV century. The points of analysis have been shown. The presence of zinc is due to later repaints (after the XVIII century). So, there could be a correspondence between the presence of zinc and the non-original component. The table gives an estimation of the presence of zinc for the different colors and for the totality of the painting.

Color	Zn presence
White	100 %
Carnations	33 %
Red	89 %
Gold-plated	33 %
Yellow	100 %
Black	80 %
Blue	75 %
Green	100 %
Total	73 %



"Virgen con Niño", wood sculpture found by the Spanish police in the illegal traffic. It is supposed to be from the romanian period. However, EDXRF analyses show the presence of zinc and barium (lithopone) and titanium (white titanium), which indicate that it was totally repainted in these last centuries.



"Pobrecitas", engraving from Goya, edition of 1970. The non-destructive EDXRF technique is able to study the composition of these delicate works. In this case, copper from the plate was not observed, which means that the edition was done after the plate was chromed, i.e., later than 1857. The EDXRF analysis is sometimes able to distinguish between an original edition and a modern one.

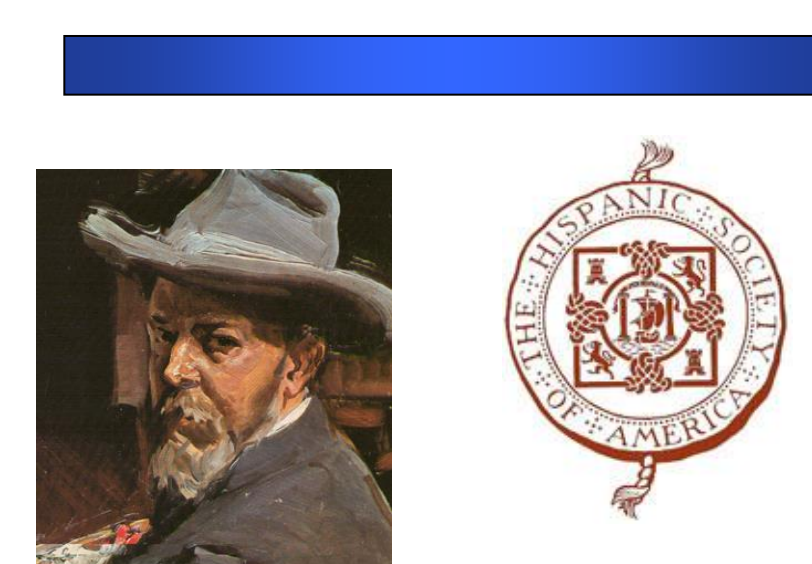
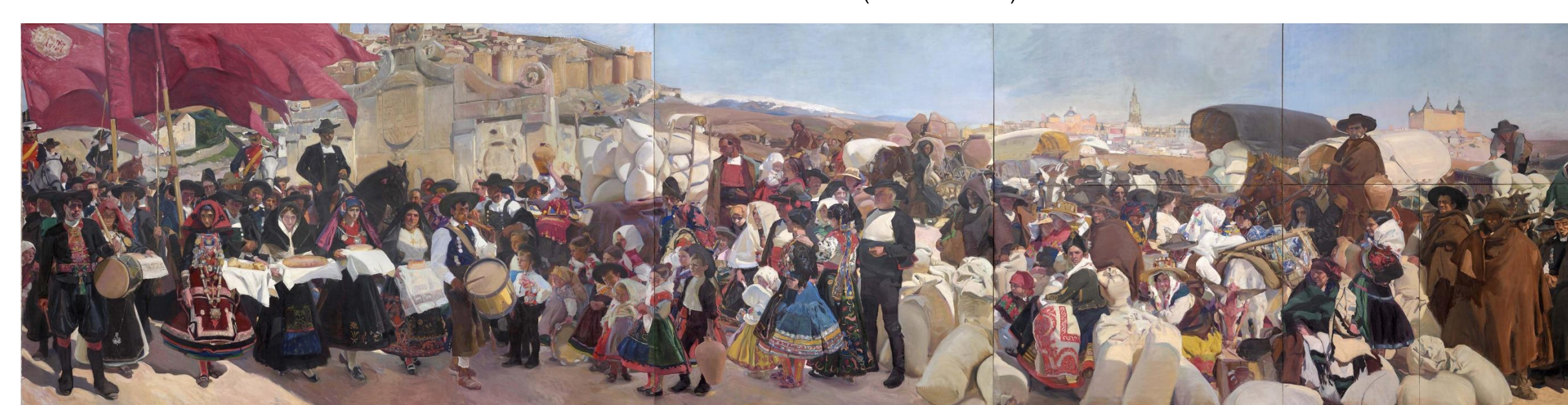
IDENTIFICATION OF PIGMENTS

Characterization of pigments present in rock art, ceramics, canvas,

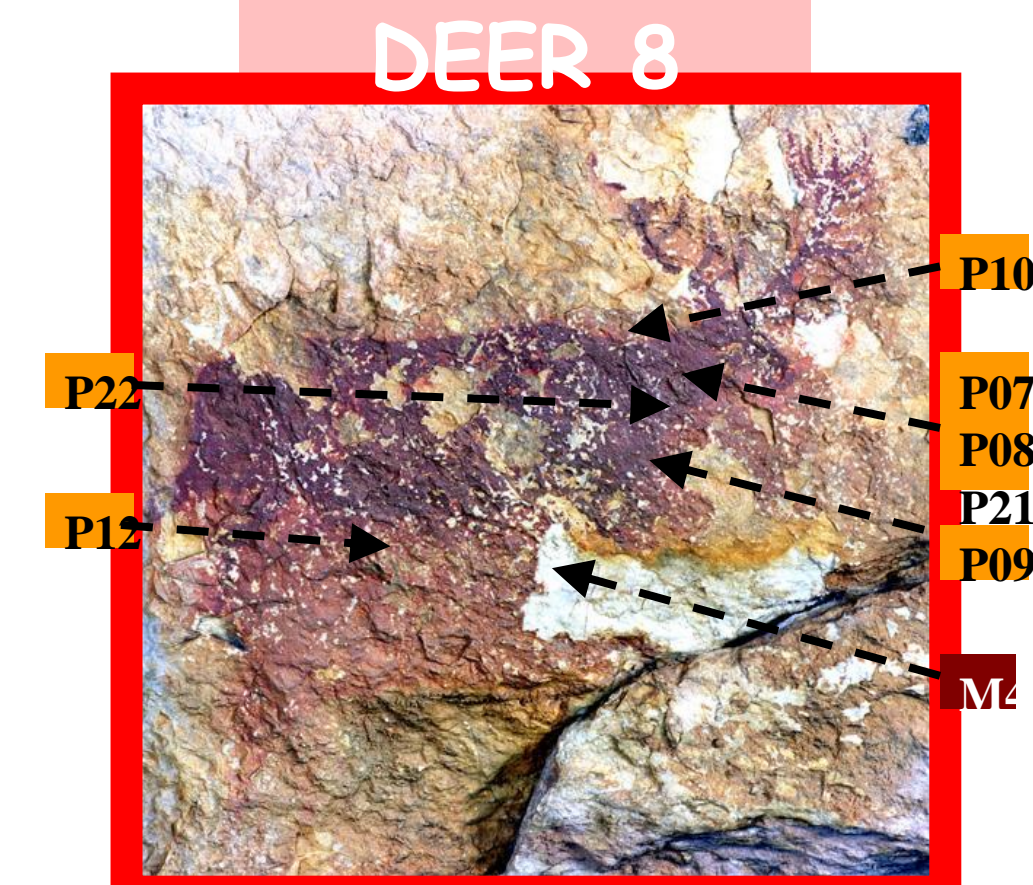
The Sorolla's "VISION OF SPAIN"

Sorolla's masterwork *Vision of Spain*, comprised of fourteen monumental oil paintings on canvas depicting the peoples and regions of Spain, has served as a highlight of the Hispanic Society's museum since. The pictorial film was prepared using both strong colour pastes and smooth, sparsely painted areas. The *Vision of Spain* has suffered the normal consequences of the aging process common amongst oil paintings dating from the beginning of the 20th century (discolouration, darkening of the paint, powdered pigments, gaps or cracks of the pigment layer, ...), also having been influenced by its large scale dimensions and its surrounding environment (dust, humidity, extreme temperatures, ...).

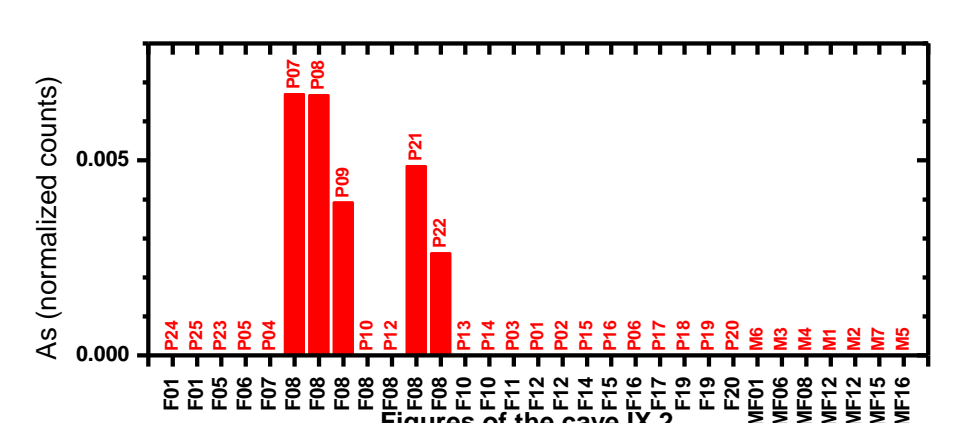
We have analyzed, by means a portable EDXRF spectrometer, a total of 609 points corresponding to the pigments and priming layers, and we have identified 27 inorganic pigments that are characteristics of the Sorollas' palette.



Rock art pigments



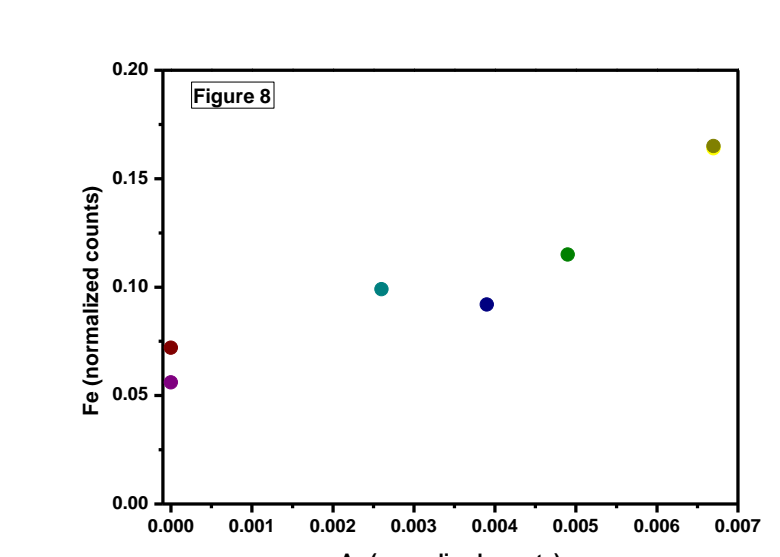
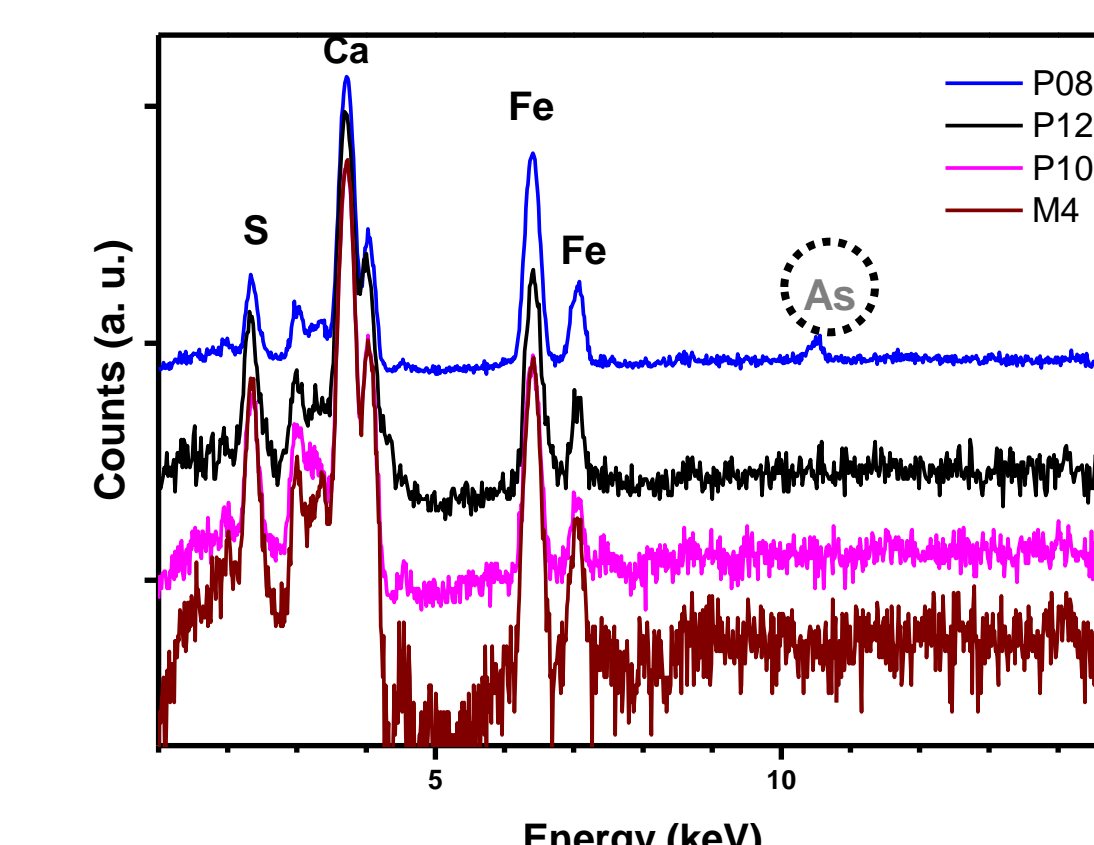
XRF spectra of different points from the deer # 8. The presence of As was only detected over a restricted zone.



Arsenic is only present in the red pigment of the deer # 8

Iron is the color-producing agent in all red paintings.

Only the deer # 8 present a singularity in the elemental composition of the red pigment



The correlation between the net area of the Fe and As peaks is an indication of the utilization of an iron mineral with arsenic traces.

THE MASTERPIECES

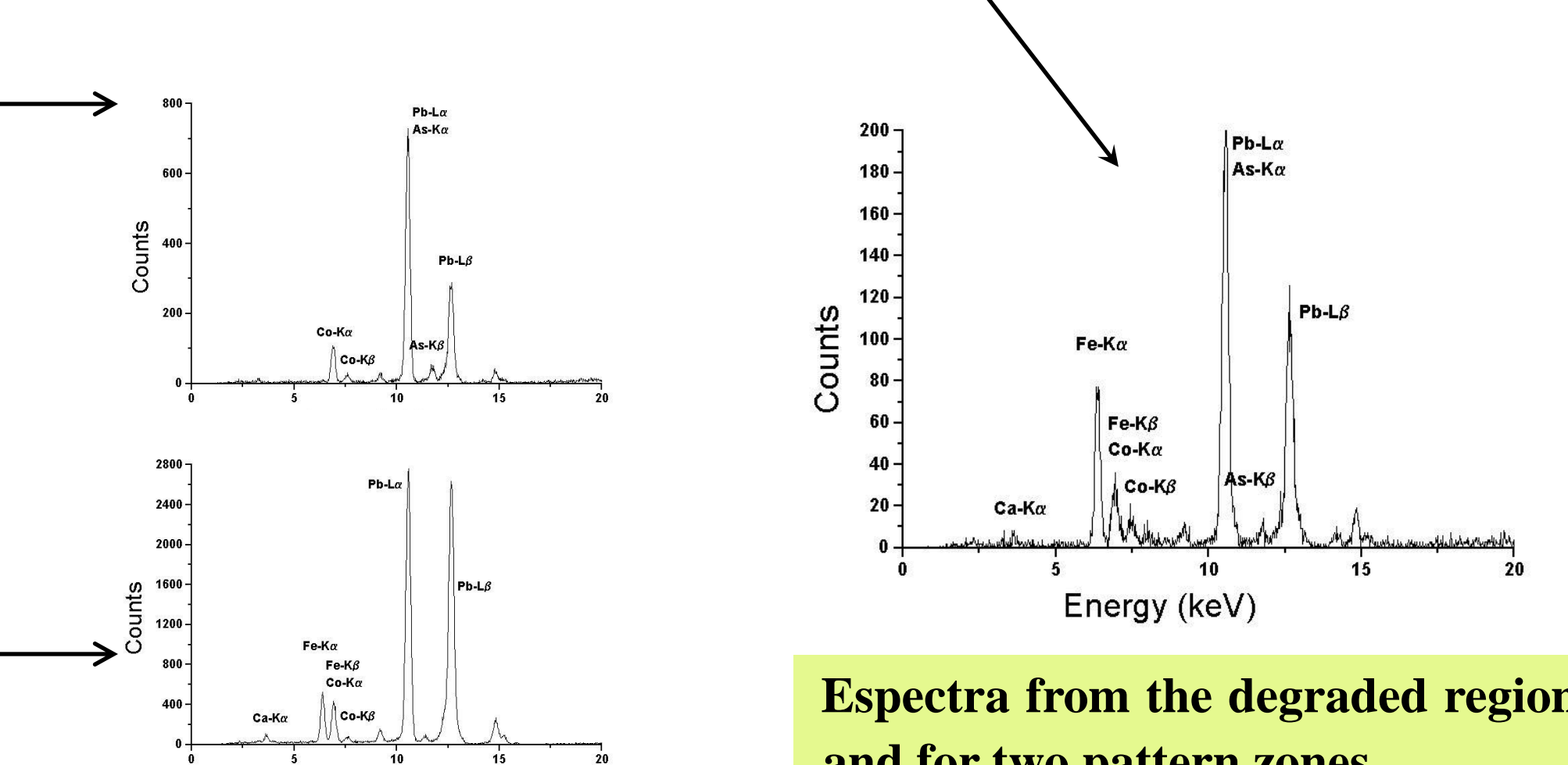
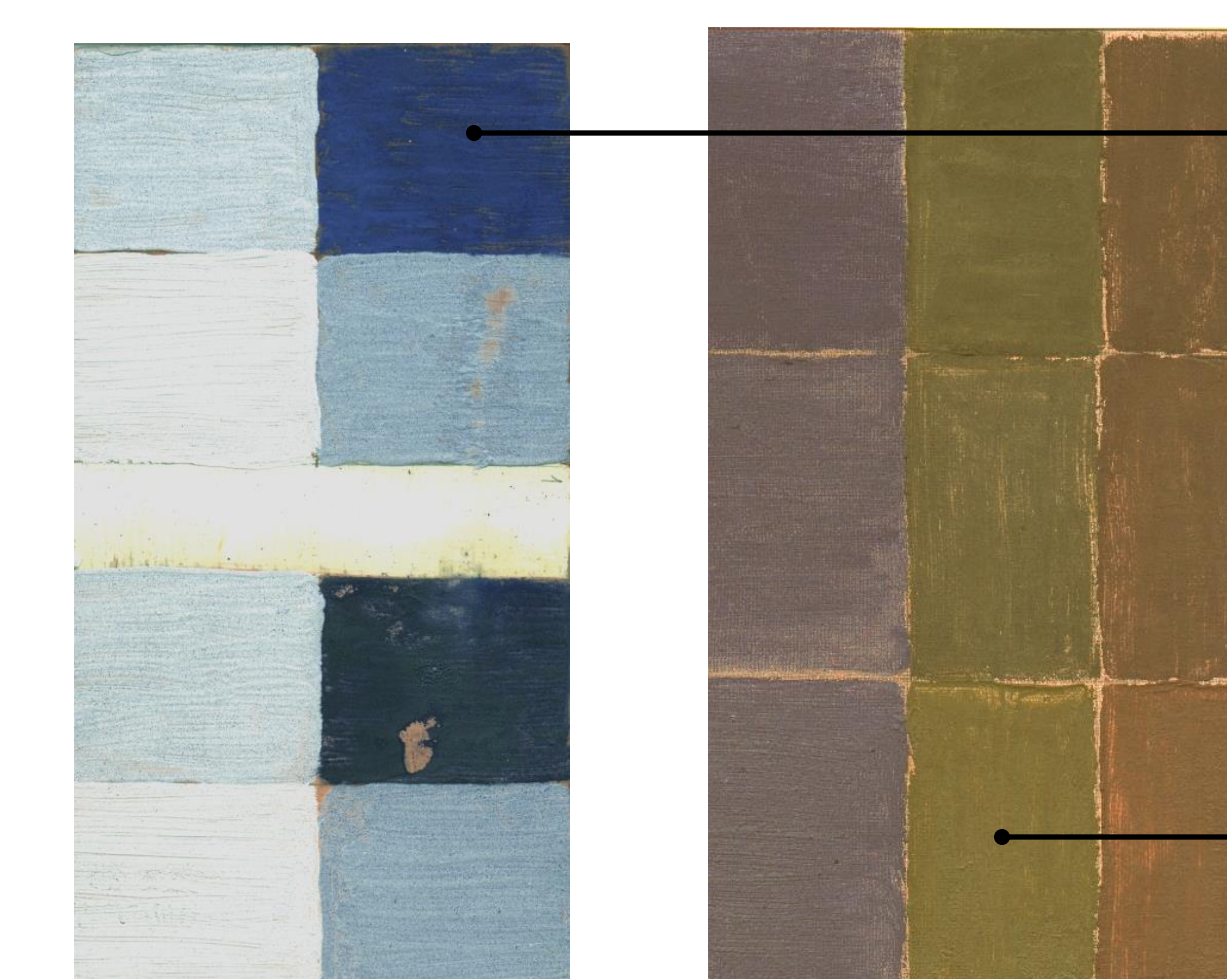
- Paintings on canvas of the University of Valencia from the XVII-XVIII century show some degraded regions.

THE PATTERNS

- Production of patterns which contain the pigments that have the same chemical elements as the degraded zone.
- Pigments and style of the XVII-XVIII century are used.



- Above left: "Coronation", (Anonymous, 1700-1750), which contains a degraded region.
- Above right: the same painting after the reconstruction of the original tonality of the degraded region.



Spectra from the degraded region and for two pattern zones.

THE METHOD

- The degraded (or discolored) regions show a variety of chemical elements representing a mixture of pigments: Pb, lead white; Co-As, smalt; Fe, iron oxides earth and Ca, calcium carbonates.
- The most probable cause for the degraded regions is the use of smalt in oil-media, according to the literature.
- Comparison of the relative abundances of the different elements from the EDXRF analyses between the degraded region of the painting and the patterns can be used to see the evolution of the tonality for the different concentration of pigments.
- The study of microphotographies of the degraded region is used to distinguish between the green and the brown regions, which are chemically similar.
- This combined procedure allows to make an estimation of the degraded region, as seen in the picture.