IDENTIFICATION OF FORGED WORKS OF ART BY PORTABLE EDXRF SPECTROMETRY

1M. Ardid, 1J.L. Ferrero, 1D. Juanes, 1C. Roldán, 2M. Crespo, 2M.E. Pernett, 3M.Marzal, 4M. Burke, 5S. Rovira, 6R. Vives

1Institut de Ciència dels Materials de la Universitat de València (ICMUV)
Apdo 22085. E-46701 VALENCIA (Spain)
2Museo Nacional de Bellas Artes, LA HABANA (Cuba)
3Servei de Conservació i Restauració de Bens Museístics, Generalitat Valenciana, VALENCIA (Spain)
4Hispanic Society of America, NEW YORK (USA)
5Museo Arqueológico Nacional MADRID (Spain)
6Dept. de Pintura, Universitat de Barcelona, BARCELONA (Spain)

ABSTRACT

The study of patrimonial works by non-destructive techniques allow the analysis of unique and historic pieces without compromising their integrity. The Archaeometry Unit of the Institut de Ciència dels Materials de la Universitat de València (ICMUV) has carried out Energy Dispersive X-Ray Fluorescence (EDXRF) analyses for the identification of forged works of art using portable instrumentation. In this work, we present two applied examples of works that were atribuited to Joaquín Sorolla. The comparison of the EDXRF spectra of these works with a database, which contains the spectra and compositions of more than 50 well-known originals, gives evidences of fakes. In addition to the detection of forged works of art, EDXRF may help to obtain information of the art pieces that could be important to determine its value. For instance, the knowledge of the degree of originality is very important. Although the authenticity of the work may be clear, it could have been degraded, repainted, or rebuilt. The EDXRF technique can help to distinguish between the original parts of the works and latter modifications. Another application is the acquisition of technological information about the process of making the work of art and the state of preservation. Finally, we will describe the method and an example of the reconstruction of the original tonality of some degraded regions in paintings from the comparison of their chemical composition with those of some produced patterns.

INTRODUCTION

The Energy Dispersive X-Ray Fluorescence is a well-established analysis technique for qualitative and semi-quantitative identification of chemical elements in works of art where the integrity of the sample is a basic requirement of the measurement. The Unitat d'Arqueometria (UA) of ICMUV has carried out EDXRF analyses on different kinds of works of art (paintings, metals, sculptures, ceramics and engravings) located in museums, churches, excavations, etc., over the whole Spanish territory and abroad [1,2]. The close collaboration with those responsible for artistic patrimony has been reflected in the elaboration of technical and analytical reports on the state of conservation, alterations, and compositions of the analyzed artistic patrimony. In this paper, we focus on the description of the EDXRF analysis as a tool that could help in determining the value of the work of art, and we present a selection of case studies carried out by the UA of the ICMUV that illustrate this application. The most immediate and exciting use in this sense is the detection of fakes. However, we should not disregard other applications that also could be important for the purpose of giving argument to value the pieces.
For instance, we can use the EDXRF analysis to discriminate between the part of a work of art that corresponds to the author, the part which corresponds to later interventions, and to obtain technological information about the process of production of a work of art and about its state of preservation. Finally, we describe the use of the EDXRF technique to reconstruct the original tonality of degraded paintings that could give a better vision of it at the time it was painted.

**EXPERIMENTAL SETUP**

A portable EDXRF system [3] integrated with commercial elements was used for the analyses [1]. The small-sized and air-cooled X-ray tube, EIS XRG35, was used for excitation. This model produces an X-ray beam from a tungsten anode filtered with a 0.3 mm aluminium effective thickness. It can operate with a tube voltage from 0 to 35 kV, and a current intensity from 0 to 0.3 mA. Aluminium and methacrylate collimators provide X-ray spots of 1, 3, and 5 mm. The emitted fluorescence radiation from the sample was registered with an energy-dispersive high-performance Si-PIN detector (AMPTEK XR-100CR) with a 7 mm² useful area, 300 µm thickness, a 25 µm light-tight beryllium window and an energy resolution of about 200 eV for 5.9 keV radiation. A small box contains a high-quality preamplifier and the Peltier circuit for the thermoelectric cooler. The output pulse produced by the amplifier is connected directly to the input of a multi-channel analyzer, AMPTEK MCA8000A 'Pocket MCA'.

The analyses were carried out operating the X-ray tube potentials, current intensity, and acquisition time that were able to excite the fluorescence lines of a wide energy range and to obtain EDXRF with acceptable statistics. The X-ray tube and the Si-PIN detector are assembled on a measurement head that allows us to place it close to the sample and to change their relative orientation.

**RESULTS AND DISCUSSION**

In this section we describe four applications mentioned of the EDXRF technique which have some importance for the determination of the value of a certain work of art and present some examples.

- **Forgeries**
  The comparison of the EDXRF composition of some works of art atributed to Joaquín Sorolla with a database, which contains the spectra and compositions of more than 50 well-known originals [2], gives evidences to discover forgeries. Here, we present two supposed forgeries:

  - **“Carros en la Playa”** from the Museo Nacional de Bellas Artes de La Habana (Fig.1). This work is signed as “J. Sorolla B.” and judging by its appearance and thematic, it could be dated between 1880 and 1890. There exists a work with the same scene, which has been confirmed that it was painted by Joaquín Sorolla, in the Caja de Ahorros KUTXA (Caja de Gipuzkoa y San Sebastián, Spain) Collection. In principle, it is not very probable that the author painted the scene twice. In addition, the EDXRF spectra show the extensive presence of titanium, but the beginning of the use of white titanium is reported between 1916 and 1919 [4]. Sorolla died in 1923 and although allowing the possibility that it might be a datation error, the comparison of the spectra with those of the database, in which titanium has not been found and zinc has never...
observed as the most important element, makes difficult to believe that it was painted by Sorolla.

- “Portrait of Two Children,” unsigned work from the Hispanic Society of America (Fig.2). Some experts have made the hypothesis that it was painted by Sorolla but the very high presence of zinc makes this unlikely, because zinc has never been found as the most important element in Sorolla's paintings.

Fig. 1. "Carros en la Playa", in which the analysis points are shown, and the analysis spectrum of point 8, in which titanium appears and zinc is the most important element.

Fig. 2. "Portrait of Two Children", in which the analysis points have been shown. The analysis spectrum of point 2 is also presented.

- **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. Here, we describe some examples.

- “Retaule de l’Altar Major de la Catedral de València,” Hernando Llanos and Yañez de la Almedina, 1507-1510. In an agreement between the authors and the owners, the use of a very expensive pigment, blue ultramar (3NaAlSiO₄Na₂S₃), was allowed. However, 10 points of different tonalities of blue have been analysed and none of them show sensitivity to sulphur and
silicon peaks. A high quantity of copper, however, is observed, which could indicate that azurite was mostly used.

- “Screws of the plates of the cupola of St. Isaac Church of St. Petersburg” (Fig. 3). The corrosion of these screws is due to the formation of compounds of copper-sulphur and copper-chlorine. The presence of mercury indicates that the technique used for gold-plating 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” [1].

![Fig. 3. Screws of the Plates of the Cupola of St. Isaac Church of St. Petersburg and an EDXRF spectrum, in which sulphur, chlorine and mercury besides copper and the gold are observed.](image)

- Degree of Originality
The EDXRF analysis can help to determine 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 of this application.

- “Fondo de Lucillo Funerario Gótico de la Iglesia de San Esteban de Cuéllar” from the Museo Arqueológico Nacional, end of the XV century. The presence of zinc in this work is due to latter repaints (from the XVIII century and latter [4]). So, there could be a correspondence between the presence of zinc and the non-original component of the work. In table 1 an estimation of the presence of zinc for the different colors, and for the totality of the painting is presented.

<table>
<thead>
<tr>
<th>Color</th>
<th>White</th>
<th>Carnations</th>
<th>Red</th>
<th>Gold-Plated</th>
<th>Yellow</th>
<th>Black</th>
<th>Blue</th>
<th>Green</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn presence</td>
<td>100%</td>
<td>33%</td>
<td>89%</td>
<td>33%</td>
<td>100%</td>
<td>80%</td>
<td>75%</td>
<td>100%</td>
<td>73%</td>
</tr>
</tbody>
</table>

Table 1. Estimated presence of zinc and, therefore, non-original component of the different colors of the painting.

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

- "Pobrecitas", engraving from Goya, edition of 1970. The non-destructive technique is able to study the composition of such 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., latter than 1857. EDXRF analysis is sometimes able to distinguish between an original edition and a modern one.

- Reconstruction of the original tonality
The EDXRF technique can be used to reconstruct the original tonality of discolored regions from the comparison of the chemical composition with patterns. Here, we present an example of degraded smalt in the painting "Coronation" (Anonymous, 1700-1750) from the collection of the University of Valencia, which is shown in Fig. 4-Left.

![Figure 4: "Coronation" showing the associated EDXRF spectrum of the degraded region.](image)

The most probable cause for the degraded regions is the use of smalt in oil-media, according to the literature [4]. The degraded or discolored regions show a variety of chemical elements representing a mixture of pigments: Pb, lead white; Co-As, smalt; Fe, earts with iron oxides and Ca, calcium carbonates. Patterns which contain the pigments that have the same chemical elements as the degraded zone are produced. We show some of them together with some spectra in Fig. 5. Pigments and style of the XVII-XVIII century has been used for the patterns. The comparison from the EDXRF spectra of the relative abundances of the different elements 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 it is shown in Fig. 3-Right.
CONCLUSION

In this work we have presented some examples of the use of the EDXRF spectrometry to obtain information that can be important to value a work of art. First, we have applied this technique to detect fakes in some paintings which could be attributed to Sorolla. The comparison of the EDXRF spectra of these paintings with a database of well-known Sorolla's paintings gives additional arguments to judge the originality of the work. The fact of detecting titanium in "Carros en la Playa" of the Museo de Bellas Artes de La Habana makes almost impossible that this painting was painted by Sorolla. In "Portrait of Two Children" we have detected zinc as the most important element, which is not observed in our database. This could indicate that this work is also a fake, although it is not a conclusive argument.

In addition, the EDXRF technique has been found to be useful in determining the degree of originality of a work of art, because it is sometimes able to distinguish between the original part from the author and latter modifications from restorations. The use of EDXRF analysis to obtain technological information of the process involved in producing the work of art for paintings and for gold-plated pieces has also been presented. Finally, we have described the reconstruction of the original tonality of a degraded region of "Coronation" by comparing its EDXRF analyses with some patterns.

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REFERENCES