EDXRF ANALYSIS OF PIGMENTS OF WORKS OF ART FROM THE SPAIN'S CULTURAL HERITAGE

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ABSTRACT

The objective of the Unit of Archaeometry (UA) of the Institute of Material Science from the University of Valencia (ICMUV) is the development of non-destructive methods for the determination of the nature, structures and components of the works of art. Taking advantage of the experience of some of their members in Nuclear Instrumentation, and with the invaluable collaboration of restorers and curators of museums, we have designed several devices for X-ray fluorescence. These devices have been adapted to the varied practical situations in the analysis of works of art for their characterization, restoration and better conservation.

INTRODUCTION

Energy Dispersive X-Ray Fluorescence (EDXRF) is a widely applied analysis technique for the identification of chemical elements in works of art where the integrity of the sample is a basic requirement of the measurement [1-3]. The simplicity of the technique that doesn't require sample preparation and the use of portable instrumentation for in situ analysis make EDXRF a useful non-destructive analytical technique for objects of historical or artistic interest. The UA of the ICMUV has as its purpose the analysis and the characterization of works of cultural interest that are part of the Spain's artistic patrimony. We use the EDXRF analysis with other complementary techniques to achieve a better knowledge of the works of art for archaeologists, restorers, curators and art historians.

The activity of the UA covers a wide field of EDXRF analysis: polychrome Iberian sculpture [5]; analysis of pigments of altarpieces from the XIV to XVI centuries [6]; analysis of painting on canvas from the XIX and XX centuries [7]; analysis of inks and alterations of documents on paper support [4]; analysis of Iberian silver work [4] and analysis of mural painting from the XIV to XVI centuries [8]. Here we present the characteristics of the EDXRF instrumentation used by the UA of the ICMUV and examples of their applicability.

MATERIAL AND METHODS

The EDXRF instrumentation consists of a X-ray source coupled to semiconductors detectors by means of a mechanical device. This allows us to choose the best option between two different configurations: a fixed one, for analysis in the laboratory of the UA; and a portable one capable of being transported to carry out "in situ" analysis.

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The EDXRF analysis system used is extremely versatile, portable, of easy operation, and it allows to carry out, in situ or in the laboratory, non destructive and non aggressive analysis and to obtain results practically in real time. In the first place we will describe the characteristics of the X-ray source and, next, we will describe each equipment configuration.

The excitation source is an X-ray tube (Oxford Instruments) that produces a X-ray beam coming from an anode of rhodium. The voltage and the current settings of the source can be varied manually between 0 and 50 kV and between 0 and 1 mA, respectively. This way the energy of those X-rays emitted is enough to excite the transitions of the lines K and L of the elements present in the sample. The output X-ray beam is collimated by a 5 mm methacryllate collimator to restrict the analysis surface on the sample. The characteristic X-ray emitted by the sample are registered by solid state detectors that we describe in the following paragraphs.

The fixed configurations is integrated by the X-ray source and two Si(Li) detectors cooled by liquid nitrogen: one of them has a resolution of 140 eV (FWHM at 5.9 keV) and the electronic signal generated in the detector goes to a pulse processor LINK 2048 and from here to an A/D converter and to a MCA that is part of the hardware of the PCA card (Tennelec Instruments) incorporated in a PC; the other one has a resolution of 170 eV (FWHM to 5.9 keV) with the electronic configuration NOMAD from ORTEC. The X-ray source and the detectors are integrated in a mechanical device that allows fixing the angle of incidence of the beam on the sample and the solid angle that the detector subtends with the direction of the characteristic X-ray emitted by the sample (figure 1).

Figure 1.- EDXRF portable configuration with Si(Li) detector. In situ analysis of the work "Christ tied to a column" (V. Macip, Museo de Bellas Artes of Valencia). A: X-ray tube. B: methacryllate collimator. C: Si(Li) detector. D: Dewar for liquid nitrogen. E: mechanical support.
These last configurations have reduced mobility because the Dewar for liquid nitrogen and are suitable for works in the laboratory and in restoration and conservation departments of museums. Figure 1 shows the fixed configuration during the analyses made in the restoration department from the Museo de Bellas Artes of Valencia.

The portable configuration is integrated by Cd(Zn)Te and Si-PIN detectors manufactured by AMPTEK. The Cd(Zn)Te detector, model XR100T-CZT, is formed by a crystal of $3 \times 3 \times 2 \, \text{mm}^3$ with a beryllium window of 250 microns, with an energy resolution of 340 eV (FWHM at 5.9 keV). The Si-PIN detector, model XR100CR, has an effective area of 7 mm$^2$, a beryllium window of 25 microns and a resolution of 220 eV (FWHM at 5.9 keV). Both detectors are thermoelectrically cooled by Peltier effect. The detectors signal are amplified by an AMPTEK PX2T amplifier and coded by an AMPTEK MCA8000 connected to a portable computer. These detectors have a poorer resolution than the Si(Li) detector but for compensation they are of reduced size, which allows to integrate them in a portable module of great maneuverability and capable for field works [9]. This configuration can be observed in figure 2 during the analysis of the mural pigments of the Chapel of Los Corporales of Daroca (Zaragoza). The Cd(Zn)Te detector has an efficiency close to 100% for energies between 20 and 40 keV and the Si-PIN has an efficiency below 30% in this energy interval. For energies below 20 keV the Si-PIN detector has better efficiency than the Cd(Zn)Te detector [2], therefore it can be used to identify high energy fluorescence peaks, while the Si-PIN is suitable to discriminate and to identify the low energy peaks.

![Figure 2](image)

Figure 2.- Portable EDXRF configuration with the Si-PIN detector. In situ analysis of the mural pigments from the “Chapel of Los Corporales” (Church of Santa Maria, Daroca).

The conditions of operation of the EDXRF equipment are preset to optimize the analyses. On one hand the source-sample-detector geometry is determined and on the other hand the acquisition
time and the potential and the intensity of current of the X-ray source are selected to excite the
fluorescence lines of a wide energy band and to obtain spectra with an acceptable statistic.

RESULTS

The EDXRF analyses that we present in this section are a sample of their applicability and they
have been selected among the wide range of applications carried out by the UA of the ICMUV.

The fixed configuration has been used to analyze the pigments of altarpieces of primitive
Valencian painters [6]: Maestro de Alcañiz, Vicente Macip and Juan de Juanes, among others.
Altarpieces of the XVI century of important authors settled in Valencia like Los Hernández
(Yañez and Llanos), whose works decorate the doors of the Main Altar of the Cathedral of
Valencia, have also been analyzed. The analyses were carried out previous to their restoration in
the restoration department from the Museo de Bellas Artes of Valencia. This same configuration
has been used to analyze the elements that compose the metallic structure of Iberian silver work
coming from archaeological excavations of the Comunidad Valenciana [4]. Lastly this
configuration has allowed the examination of the composition of inks of a document of the XVI
century certified by a notary and the alterations of an engraving of the XIX century [4]. The
EDXRF analyses of silver work and paper were made in the laboratories of the UA since the size
of the analyzed works allowed their transfer without risks for their integrity.

The portable configuration of the fluorescence equipment has been employed for its easy
transport on those occasions that the analyses were made on works whose accessibility was
severely limited or in those other cases where it was necessary to travel long distances. As an
example of the first case we show the EDXRF analyses made on mural paintings of the Chapel of
Los Corporales of Daroca (Zaragoza) [8] with the analysis equipment on the top of a scaffolding
of five meters over the floor level. An example of the second case is the analysis of the pictorial
work of Joaquin Sorolla. The analyses were carried out by the UA in the Museo Thyssen-
Bornemisza of Madrid during the exposition in their exhibition rooms [7]. Other examples are the
analyses of pigments from the Dama de Baza, one of the more representative sculptures of the
Iberian art (IV century B.C.), and the analyses of Iberian pigments [5]. These analyses were
carried out in the Museo Arqueologic Nacional (Madrid) and the Museo Monografico La
Alcudia (Elche Alicante) respectively.

A sample of the characteristics of the EDXRF spectra that are obtained with the two analytic
configurations can be observed in figures 3 and 4. In figure 3 we show a high resolution EDXRF
spectrum of the ochre pigment of the altarpiece "The Adoration of the Shepherds" painted by
Vicente Macip in 1529. In this figure we can observe the excellent energy resolution of the Si(Li)
detector that discriminates against the fluorescence lines of different elements. In the spectrum of
the figure 3 we have identified the presence of arsenic from the fluorescence lines Kα1.2 (10.53
keV) and Kβ1.3 (11.70 keV). The line Kα1.2 of the arsenic is superimposed to the line Lα1.2 (10.54
keV) of the lead. The degradation noticed in the ochre pigment can be explained from the
EDXRF analysis by the incompatibility among lead compounds (white lead) and arsenic
compounds (oropimente or rejalgar).
Figure 3.- EDXRF spectrum obtained with the Si(Li) detector of an arsenic based ochre pigment from the work "The Adoration of the Shepherds" (V. Macip, 1529; Museo de Bellas Artes of Valencia). The Kα₁,₂ (10.53 keV) arsenic fluorescence line is overlapped with the Lα₁,₂ (10.54 keV) lead line.

Figure 4.- EDXRF spectrum obtained with the Cd(Zn)Te detector of a lead-tin yellow pigment from the work "The Adoration of the Three Wise Men" (V. Macip, 1543; Museo de Bellas Artes of Valencia).
The figure 4 corresponds to a EDXRF spectrum obtained with the Cd(Zn)Te detector of a yellow pigment of the work "The Adoration of the Three Wise Men" (V. Macip, 1543). This pigment has been identified as lead-tin yellow from the fluorescence lines of the lead and tin. We have used the Cd(Zn)Te detector for their high efficiency in the detection of the Kα line of tin. In this figure the worst energy resolution in the peaks can be observed in comparison with the spectrum of the figure 3.

As conclusion we want to emphasize that the utilization of the EDXRF spectrometers based on configurations as those we employed could be an easy tool for investigation in the field of the restoration and conservation of works of art [9-10].

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