DESIGN OF EDXRF EQUIPMENT FOR THE NONDESTRUCTIVE STUDY OF PRINTS


1Instituto de Ciencia de los Materiales de la Universitat de València (ICMUV) Apdo. 22085. E-46701 Valencia (Spain) E-mail: jose.ferrero@uv.es
2Desarrollo y Aplicaciones Científicas y Técnicas S.L. Parque Tecnológico. CEEI-Valencia. Centro de Negocios. C/ Benjamin Franklin, 12 E-46980 Paterna (Spain)
4Departament de Pintura. Universitat de Barcelona (Spain)
5Museo Provincial de Teruel (Spain)

ABSTRACT

Because of the fragility and size of the old master prints and the impossibility to take representative samples, there are no exhaustive studies of the analytical scientific constituent materials. Investigations have been made mainly on the basis of the documentation and conservation. In order to complement these studies with the analytical aspect, the Unidad de Arqueometría (UA) of the Instituto de Ciencia de los Materiales (ICMUV) of the Universitat de València, has developed Energy Dispersive X-Ray Fluorescence (EDXRF) equipment, applied to the art work analysis. This technique provides a global analysis in real time. The EDXRF system is integrated with a X-ray tube and two detectors. The first detector has high energy resolution, and the second one has high efficiency. The use of both detectors allows us to study the presence of a broad range of chemical elements. The data acquisition is made simultaneously with both detectors. In the second part of the paper, we look at some applications of this equipment. First, we present the analysis of the engraving Les hêbreux quittent l'Égypte by Johannes Wierix (third plate at the Humanae Salutis Monumenta of Arias Montanus, Anvers: Christophe Plantin, c.1575). Finally, and since the equipment can also analyse flat surfaces of objects, we present the analysis of the Iberian work craft Tesera de Hospitalidad: Caballo de Caminreal.

INTRODUCTION

Old master prints are probably the works of art least studied from the point of view of analytical scientific investigation of the constituents. They are fragile and delicate works of art due to the paper support and the process involved, which uses ink, paper and plate to produce multiple copies. These characteristics make it very inappropriate to take representative samples and for this reason there are no exhaustive studies on the nature of the constituent materials. As reported by Klockenkämper et al. [1], some analytical methods have been attempted, but in most of the cases they need considerable expenditures of time, money, and skills. However, the main drawback is that a small sample amount of these valuable works of art has to be removed. In the same reference, a new method using TXRF analysis is presented, which results in a considerable reduction of the damage since the sample is taken by rubbing a dry cotton wool.
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The difficulties of the analysis result in the fact that most of the investigations of prints are focused mainly on the documentation and conservation aspects. However, information on the constituents would be very useful to complement these studies, and for this purpose we have developed equipment especially designed for nondestructive study of prints at the Archaeometry Unit of ICMUV. It is based in the Energy Dispersive X-Ray Fluorescence technique, which appears like a suitable tool to make this kind of complementary analysis [2].

In this article we describe the equipment, we present the analysis of the engraving *Les hêbreux quittent l’Egypte* by Johannes Wierix as an application of this instrumentation on prints, and finally we consider other possible applications, describing, as an example, the analysis of the bronze piece *Tesera de Hospitalidad: Caballo de Caminreal*.

THE EQUIPMENT

With respect to previous EDXRF designs [2,3], this equipment has been especially designed to enhance the possibilities of the EDXRF analysis of prints. It consist of a X-ray tube (EIS S.r.l.) with Palladium anode that works to a variable potential of 0 to 35 kV and a variable intensity from 0 to 1 mA, and provides a collimated beam of 2 mm of diameter, and two detectors. The first one is a Si-PIN detector (Röntec Inc.) with a 8µm light-tight beryllium window and an energy resolution of about 190 eV for 5.9 keV. The second one is a high efficiency CdTe detector (Amptek Inc.) with an energy resolution of about 1.2 keV for 122 keV. The Si-PIN allows us to detect the presence of light and medium mass-elements in the zone of analysis. The engravings cannot be analysed in vacuum, so it is very difficult to detect the heavy elements from low energy X-ray fluorescence lines. The CdTe detects the presence of these elements through high energy X-ray fluorescence lines. The data acquisition is able to take and show the data from both detectors simultaneously. The scheme of the two possible options to present the data is presented in Figure 1. The X-ray tube and the detectors are mounted in a mechanical support. The geometry of the three elements has been optimized to minimise the background in the recorded spectra. In addition, there is a video camera which allows us to position the print and select the zone that is going to be analysed. The pictures are also useful to catalogue better and easier the analysed points and the spectra in a database. Finally, there is a computer, which controls the acquisition and saves the data.

![Figure 1. Scheme of the data acquisition system for both detectors](image)

A general view of the equipment can be seen in Figure 2. In the left picture we can observe the different elements, from left to right, the computer, the electronics of the data acquisition
system and the box with the EDXRF equipment, which contains the X-ray tube, the two detectors and the video camera. On the right, detailed views of the irradiation zone from outside and inside of the box are also presented. With these pictures we would like to show the distribution of the different elements, give an idea of the dimensions, and show how the print is positioned.

![Equipment and Irradiation Zone](image)

Figure 2. General view of the equipment and details of the irradiation zone from outside and inside views.

We would like to point out some features of the equipment which allow it to have a higher yield of analysis with respect to previous EDXRF spectrometers [2,3]. The combination of detectors makes it possible to detect low and high energy photons (with the high resolution Si-PIN and the high efficiency CdTe detectors, respectively). Therefore, a wide range of elements can be detected despite the presence of air. High yields are obtained, which is very convenient to study fragile work of art. Both detectors are integrated by the same data acquisition. The mechanical support maintains the geometry fixed, and then it is very easy to make comparative studies. This is essential for analysing prints, not only because the study of inks are done by comparing zones with and without ink, but also because the prints are analysed in different campaigns, the results of which have to be compared. Moreover, the main aspects to be investigated are the knowledge of the general features of different prints concerning the paper, ink and plate, and, on the other hand, the particular characteristics of each one. Both, general aspects and unique details are usually the most important conclusions of this kind of analysis. Last, but not least, the equipment is also helpful to study any kind of flat object, not only prints, so it could have multiple applications, as we will see.

**APPLICATIONS ON OLD MASTER PRINTS**

The limitations of usual portable EDXRF spectrometers for analysing prints was the main motivation for developing new equipment more adapted for prints. For instance, one of the main drawbacks of previous spectrometers was the impossibility to maintain the geometry fixed, and, therefore, it was very difficult to extract general characteristics of prints, obtain comparable results, and make a reference database. On the other hand, the yield of Si-PIN
detector above 20 keV was sometimes not enough to detect the presence of some elements like Sn, Cd, Ag in prints. For example, in the analysis of the French print *Hispaniolae Cubae*, map by Ortelius Abraham s. XVI (Collection of Museo Nacional de Bellas Artes de La Habana, Cuba), we observed a little peak in the Sn-Kα region, but the statistics was so limited that we could not certify the existence of tin in the print. Here, we would like to remark that the opportunities for analysing such valuable works of art are unique, and therefore, it is very important to have good equipment to obtain results with enough accuracy. All these drawbacks are, in a large extent, improved with the new equipment.

Figure 3. The old master print *Les hébreux quittent l’Egypte*, in which the analysis points are shown. The video camera picture taken during the analysis of point 2 is presented. The spectra obtained with both detectors in all the three points are also shown.

Next, we describe, as an example, the analysis of the engraving *Les hébreux quittent l’Egypte* (c.1570) by Johannes Wierix [4]. We have analysed three different zones: the edge of the paper, the margin of the paper and an ink-zone of the engraving. The points of analysis are shown in Figure 3 together with the spectra for both detectors. The geometry, the excitation potential and the current intensity of the X-Ray tube (35 kV and 0.01 mA, respectively), and the time of acquisition (300 s), has remained constant in all the cases. So, we can directly compare all the analysed points. Looking at the spectra, we clearly see that the Si-PIN detector has better resolution. The Zr peak in the Si-PIN spectra comes from the zirconium in the
collimator of the detector. Here, there is another reason for having two different detectors: the combination of detectors helps to discern if one element provides from the detector equipment or from the sample. In this case, for example, we could erroneously think that a siccative containing zirconium was used, however the second detector proves that it is not the case. The Pd-Compton is another large peak present in the spectra due to the equipment. The source of this peak is the compton scattered rays of Pd-Kα photons from the anode of the X-ray tube. On the other hand, the Ar-Kα provides from the argon of the air. Notice that the intensities of these equipment related peaks are nearly independent of the point analysed, and the reason of having relatively very high peaks is found in the low yield for prints. The elements which have been found in the print are gold, copper, calcium, iron and postassium. The main results derived from the analysis are that the edge was golden as seen in the analysis of point 1, and that there is a higher presence of copper in the ink zone, as observed in the comparison of points 2 and 3. The presence of gold is proof that the item is a page of an ancient and precious book. On the other hand, the presence of copper is probably due to a migration of the worked plate to the print through the ink. This effect has been reported before in different prints, especially in the case of using new plates with deep scratch lines [2].

OTHER APPLICATIONS

The equipment is not only useful for prints but also for any kind of flat objects or small pieces. For instance, we have used it to analyse different works of art: metal plates, coins, ceramics, paintings, jewellery, etc. This tool, together with previous portable EDXRF spectrometers of the Unidad de Arqueometría of ICMUV [5,6] allow us to adapt the EDXRF technique to the particular characteristics and needs of the different kind of works of art to be analysed.

As an example, we present the analysis of the bronze Iberian work craft Tesera de Hospitalidad: Caballo de Caminreal (Teruel, Spain, s. II AC). The piece, the video camera picture and some recorded spectra can be seen in Figure 4. The comparison of the EDXRF spectra with those of known alloys allows us to quantify its composition. This piece is an alloy of around 90% copper, 10% tin, and 1% lead. The presence of calcium is due to surface impurities. Notice the high yield obtained for the Kα line of Sn in the case of CdTe detector, which is approximately ten times higher than the Si-PIN detector. This high efficiency of the CdTe detector for X-ray energies higher than 20 keV makes possible to have good yields in this region, even in the case of working with thin layers and short times of exposure, which is the case of prints. Finally, we would like to point out that in the spectra of Figure 4 the peaks related to the equipment do not appear. This is due to a higher yield of the sample, and therefore, a smaller time of exposure is needed.

CONCLUSIONS

In this work we have presented the new equipment, especially designed to do EDXRF analysis of prints. It allows us to do an analytical scientific investigation of the constituents of these fragile and delicate works of art without any damage. The main characteristics of the equipment are that elements heavier than aluminium are detected with relatively high yields. Therefore, analysis in real time can be done. A data acquisition system has been designed using standard NIM electronics to control and monitor both detectors simultaneously.
Figure 4. The Iberian piece Tesera de Hospitalidad: Caballo de Caminreal, the video camera picture taken during the analysis and some spectra obtained with both detectors are shown.

This equipment is very useful to do comparative studies and it can be applied for any kind of flat object, and not only prints. We have presented some applications in works of art.

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