PRAMANA — journal of physics | © Indian Academy of Sciences | Vol. 76, No. 2, February 2011, pp. 313–319

Portable energy-dispersive X-ray fluorescence equipment for the analysis of cultural heritage

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Abstract. Energy-dispersive X-ray fluorescence (EDXRF) especially in its portable version, generally characterized by a small X-ray tube and a Si-PIN or Si-drift detector is particularly useful to analyse works of art. EDXRF technique is nondestructive, noninvasive and multielemental. A variety of works, such as paintings of all types (including frescos and illuminated manuscripts), bronzes and brasses, gold alloys, silver alloys, ceramics, porcelains and faiences, papers, ink, stones of all types (marbles, obsidians etc.), stamps, etc. can be studied using a portable EDXRF equipment. In this paper, examples are given for analysis of the works of art with a portable EDXRF equipment.

Keywords. Energy-dispersive X-ray fluorescence analysis; works of art; paintings; alloys.

PACS Nos 78.70.En; 82.80.Ej

1. Introduction

Cultural heritage needs to be preserved, conserved, and restored from time to time. Before or during the restoration process it can be analysed. It is in fact useful to know its nature and composition, not only for a conscious restoration, but also for identifying fakes or ancient restoration areas.

The ideal analytical technique for analysing the works of art should be: (a) nondestructive and noninvasive, (b) multielemental, (c) able to analyse all elements of the periodic table and to determine the related chemical compound, (d) sensitive, reliable and sufficiently rapid, (e) able to give information *in situ* and *on-line* and (f) able to analyse objects of all types, shapes and dimensions.

Energy-dispersive X-ray fluorescence (EDXRF) analysis satisfies many of the above cited requirements; it is nondestructive and noninvasive, multielemental, sensitive, reliable and sufficiently rapid, able to carry out measurements *in situ* on objects of all types, and to deduce information practically *on-line*. However, it can neither analyse low atomic number elements (up to about $Z \sim 15$) nor identify chemical compounds.

It should be pointed out that a portable EDXRF equipment is in many cases mandatory for analysing works of art, because generally the work of art cannot be moved from museums, churches, excavation sites and so on. In this paper portable EDXRF equipments and their applications for analysing cultural heritage will be discussed.

2. Experimental set-up

An EDXRF equipment is composed of an X-ray source, an X-ray detector and a pulse-height analyser. A portable EDXRF equipment should be of smaller size and light-weight. For this reason, a radioactive source or a small size X-ray tube may be employed, coupled with a Si-PIN or a Si-drift X-ray detector. Considering the elements to be analysed and their concentration in typical works of art, the following equipments are currently suggested:

– a small size and low power X-ray tube, working at about 40 kV maximum voltage, and about 100 μA of maximum current; the X-ray tube anode should be selected according to the specific problem;

Figure 1. Portable EDXRF equipment, composed of a mini-X-ray tube with Ag anode, working at 40 kV maximum voltage and 100 μA current, and of a 123Si-drift detector. Both X-ray tube and detector are manufactured by AMPTEK Inc. Bias supply for the X-ray tube is inserted in the X-ray tube case; both amplification circuits and pulse height analyser are in the 123 module [1].

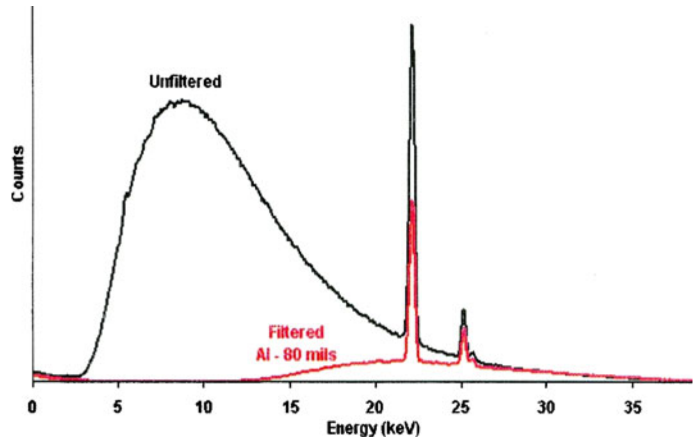

Figure 2. X-ray spectrum of a mini-X Ag anode X-ray tube at 40 kV, unfiltered and filtered (red curve) with 2 mm Al. For analysis of elements, for example Ag or Sn, only the last part of the spectrum is useful for excitation. The unfiltered first part only contributes to the background.

– an Si-drift detector, Si with a thickness of about 400–500 μm, and an energy resolution of about 130–150 eV at 5.9 keV;

– a pulse height analyser of small size.

Filtering of the X-ray tube output should be done according to the elements to be analysed. When elements emitting low-energy photons (typically from 2 keV to about 5 keV) are analysed, filtering should be avoided. On the contrary, when elements emitting X-rays from about 5 keV to about 35 keV are analysed, filtering is needed, and sometimes mandatory, to eliminate the low-energy tail of the incident X-ray spectrum, which only contributes to the background.

Collimation of both X-ray tube and detector is in any case useful; the X-ray tube collimation should be carried out according to the area and concentration of the element to be analysed. The detector should be weakly collimated, only to avoid scattered photons in the detector. Figure 1 shows a portable EDXRF equipment with these characteristics, and figure 2 shows the emitted filtered (red colour) and unfiltered X-ray spectrum [1].

3. Results

3.1 *Paintings and frescos*

EDXRF analysis of paintings and frescos can give the following information:

– presence of elements on the surface due to pollution (typically sulphur and chlorine) [2];

– identification of pigments used by the artist;

– identification of fakes, in special cases [3]; and

– identification of restored areas through the presence of 'modern' pigments [4].

An example of fake identification is given in figure 3.

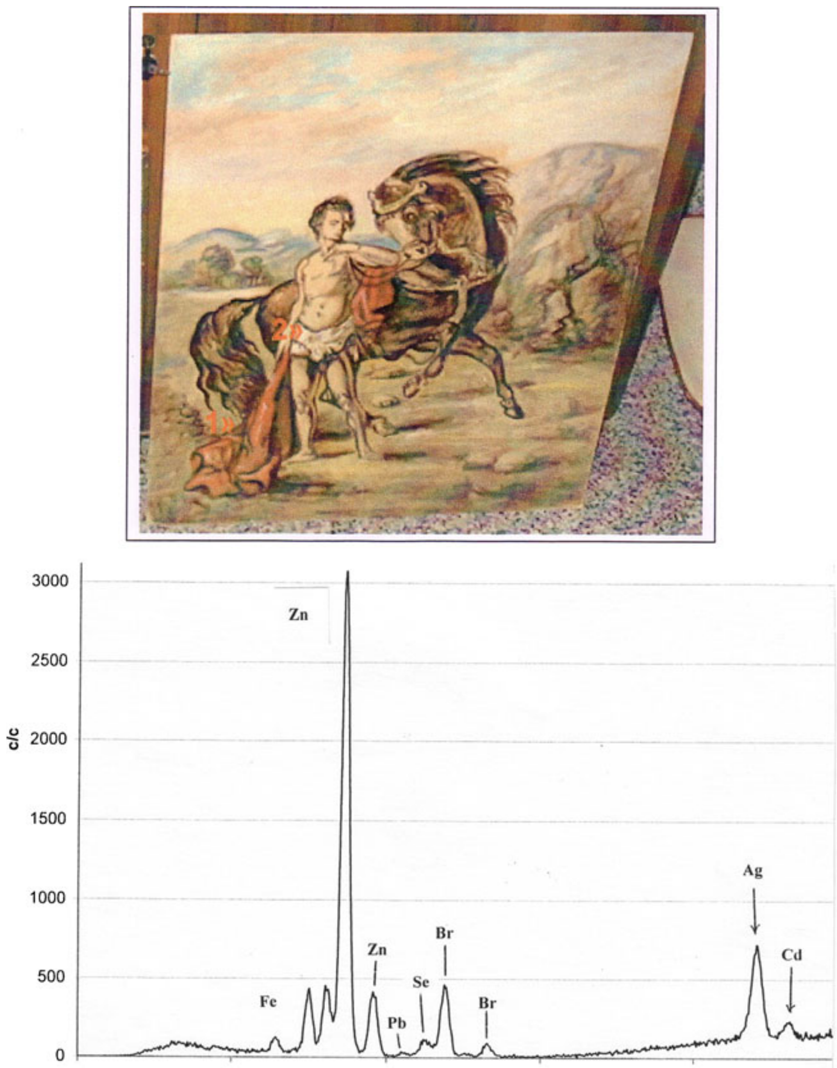

Figure 3. X-ray spectrum of the red area of the painting supposed to be of Giorgio De Chirico. The presence of Cd–Se red, which was never employed by De Chirico, at least in the period in which the painting was supposed to be made, supports the hypothesis that the painting is a fake.

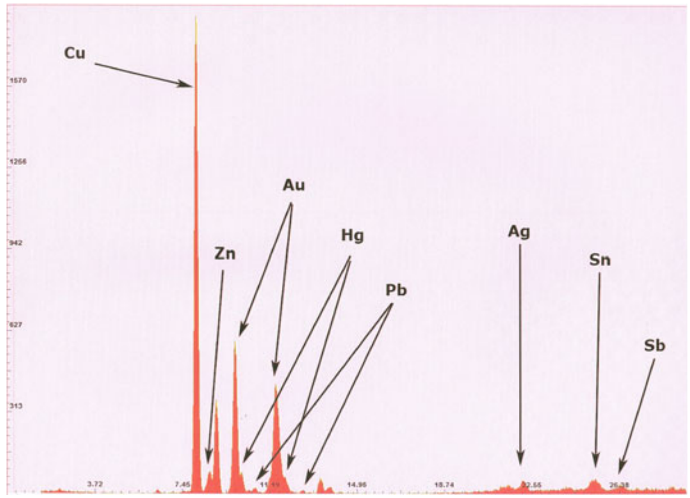

Figure 4. X-ray spectrum of a gilt bronze area of the panel Abraham from the bronze door 'Gates of Paradise' of the baptistery of Florence, by Lorenzo Ghiberti. From the altered K_α/K_β ratio of Cu, the gilding thickness may be calculated.

3.2 *Bronzes*

In the case of bronze, the area to be analysed must be cleaned, to avoid the analysis of corrosion areas or patinas. The analysis of the panel Abraham (N.4) of the 'Gates of Paradise', done by Lorenzo Ghiberti between AD 1426 and AD 1452 can be shown as an example. The panel is on gilt bronze, however the lateral sides are not gilded and the bronze is relatively clean. From the EDXRF analysis (see figure 4) the mean bronze composition was deduced as [5]:

$$\text{Cu} = 92.4\%, \quad \text{Sn} = 1.8\%, \quad \text{Pb} = 0.7\%, \quad \text{Zn} = 3.8\%,$$
$$\text{Sb} = 0.9\%, \quad \text{As} = 0.2\%, \quad \text{Ag} = 0.2\%.$$

The EDXRF analysis of gilt bronze could also be employed to deduce the mean gilding thickness which is $3.3 \pm 0.3\ \mu$m.

3.3 *Pre-hispanic gold from the north of Peru*

A large number of gold objects have been analysed, from various pre-hispanic cultures of the north of Peru [6]: Chavín (1200–200 BC), Vicús (200 BC–AD 300), Moche (400 BC–AD 700), Sicán (AD 700–1375). The evolution of the metallurgy seems to be clear: from Au–Ag alloys (with almost no Cu) of the Chavin, to Au–Ag–Cu alloys employed by Moche and Sican; from laminated gold to tumbaga, where the last object is a poor gold alloy (typically 10–20% Au, 80–90% Cu) enriched at the surface by a process called depletion gilding.

Figure 5. Moche mask from the Museum 'Tumbas Reales de Sipan', Lambayeque, Peru. A quite similar mask, from the Museum Enrico Poli in Lima, was also analysed. The X-ray spectra from the two masks are quite similar (see also table 1). The two masks were possibly manufactured contemporaneously by the same artist.

Examples of particular interest are the two Moche masks which are similar, one at the Museum 'Tumbas Reales de Sipan' [7] (figure 5) and the other at the private Museum Enrico Poli in Lima [8]. The first mask was analysed years ago, and it was showed that the mask, composed of a front side soldered with a rear side, was characterized by Au-richer front side. One of its eyes is of silver and the other is of copper. The mask at the Enrico Poli Museum was analysed recently, and it looked similar, but both eyes are of silver. The composition of the two masks is summarized in table 1.

Acknowledgements

This work was partially supported by the CNR (Consiglio Nazionale delle Ricerche, Programma Finalizzato 'Beni Culturali'), and performed within the framework of IAEA-CRP

Table 1. Compositions of Sipan and Poli masks.

	Front side Sipan mask	Front side Poli mask	Rear side Sipan mask	Rear side Poli mask
Au (%)	75	73.5	61	60.5
Ag (%)	23	24	24	28
Cu (%)	3	2.5	15	10.5

(G4.20.02/1371) 'Unification of nuclear spectrometries': integrated techniques as a new tool for material research'. The authors acknowledge A D Bustamante and J S Fabian of the 'Universidad Nacional Mayor de San Marcos', Lima, Peru, C M Calza, Dos Anjos and R T Lopes from the COPPE, Universidade Federal do Rio de Janeiro, Brasil and W Alva, L Z Chero, M C Espinoza Córdova, R Gutierrez Vasquez, R Rodriguez Ruiz and M Seclen Fernandez from the Museum 'Tumbas Reales de Sipan', Lambayeque, Peru and Marcia A Rizzutto from the USP Sao Paulo, Brasil, for cooperation in the measurements carried out in this Museum. Mr Enrico Poli, from the private Museum Enrico Poli in Lima is acknowledged for allowing to analyse many important gold and silver pre-Columbian objects. Dr Stefano Ridolfi is acknowledged for providing several standard samples of gold alloys, and for useful discussions.

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