



X-ray fluorescence analysis of yellow pigments in altarpieces by Valencian artists of the XV and XVI centuries

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Abstract

XRF analysis has allowed a quick and precise detection and identification of the inorganic elements that compose the yellow pigments in altarpieces of the XV and XVI centuries painted by the Valencian artists Miguel Alcañiz, Vicente Macip, Juan de Juanes, Hernando Yáñez de la Almedina and Hernando Llanos. The analyses have been carried out with an XRF portable system that consists of a tube of X-rays and detectors of Si(Li) and cadmium zinc telluride. This system has enabled a non-aggressive and non-destructive analysis of many pieces at the Museo de Bellas Artes of Valencia (Spain). Among the yellow pigments we have identified a pigment composed by lead and tin oxides named lead–tin yellow (Pb_2SnO_4), frequently used in European paintings from the XIV century until the first half of the XVIII century. This fact demonstrates the influence of elements and pictorial techniques from Europe to the region of Valencia. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The integrity of the works of art is the main premise that should guide the professional work of art restorers and conservators, and it should also be a norm for the techniques used to characterize them. There are non-destructive and non-aggressive analytical techniques like the X-ray fluorescence analysis (XRF) that, without attacking or destroying the work provides valuable qualitative information about their elementary chemical components [1]. In addition, the configuration of a portable and easy operation equipment which

can be transported from the laboratory to the museum, avoiding any transport of the museum objects in the other direction, has obvious advantages for the integrity of these objects. For this purpose portable XRF systems have been widely used [2–4].

This paper has two objectives. The first is to present a simple, inexpensive and portable XRF system, developed by the Archaeometry Unit of the Instituto de Ciencia de los Materiales de la Universidad de Valencia (ICMUV), that consists of a small size X-ray tube (0–50 kV, 1 mA), a high resolution Si(Li) cryogenic detector, a Peltier cooled cadmium zinc telluride detector, and modular electronic components to process the detector signals. With these elements we have carried out non-aggressive and non-destructive “in situ”

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analysis of the paintings at the Museo de Bellas Artes of Valencia.

Our second objective is the analysis, with this XRF system, of the yellow pigments used by the most important Valencian painters of the 15th and 16th centuries, Miguel de Alcañiz, Vicente Macip, Juan de Juanes and the Castilian painters who settled in Valencia, Hernando Yáñez and Hernando Llanos. An extensive study with physical and chemical analysis carried out by Kühn [5] shows that the lead–tin yellow pigment, in disuse from 1750, was frequently used by Italian, Flemish and German artists from 1300. This work reports that the lead–tin yellow pigment was also used by painters established in Valencia (Eastern coast of Spain) during this period. We also present the element identification of some degraded ochre pigments used by the above cited authors.

2. Material and methods

Pigment identification was achieved with an XRF system integrated by a small size X-ray tube (Oxford Instruments, model XTF5010) that produces a beam of X-rays coming from an anode of rhodium. The voltage and current intensity of the X-ray source are continuously variable from 0 to their maximum values, 50 kV and 1 mA. The energy of the produced X-rays are large enough to excite the characteristic K and L X-ray lines of the elements present in the samples with atomic number greater than that of sodium. The beam is collimated by a methacrylate system that produces a spot of 5 mm.

The excited X-rays are emitted from the sample and collected by a high resolution Si(Li) detector of 30 mm² (Oxford Instruments) with a FWHM of 140 eV at 5.9 keV. The detector has a beryllium window of 5 mm in diameter and 8 μm of thickness and is refrigerated by liquid nitrogen. The electronic signal coming from the detector goes to a pulse height analyzer Link 2048 (Oxford Instruments).

We also use a Peltier cooled cadmium zinc telluride (CdZnTe) detector, model XR-100T-CZT, manufactured by AMPTEK Inc. with a FWHM of 340 eV at 5.9 keV. The CdZnTe detector

(3 × 3 × 2 mm³, with a beryllium window of 250 μm), preamplifier and cooler system are integrated in a module of 15 cm × 5 cm × 3 cm. The power supply and shaping amplifier AMPTEK model PX2T-CZT provides the DC voltages needed for operation and signal processing. The CdZnTe detector has an efficiency greater than the Si(Li) detector for X-ray energies from 20 to 40 keV.

The signal output from the Link 2048 or the PX2T-CZT modules is connected directly to a multi-channel analyzer (MCA) in the PCA2 card (Tennelec Instruments) installed in a PC. The X-ray source and both detectors are integrated in a mechanical device that allows the fixing of the incidence angle of the beam and the solid angle that the detector subtends with the direction of the characteristic X-rays emitted by the sample.

This XRF equipment (Fig. 1) is a portable and easy-to-handle that was taken to the exhibition galleries and to the department of restoration at the Museo de Bellas Artes of Valencia to carry out the “in situ” analysis of the paintings.

When the painting is covered with a varnish layer the low energy fluorescent radiation is attenuated and will produce a very low signal in the detector. In these cases we carry out only the analyses of the high energy transitions and use the CdZnTe with high tube voltages. To analyze and identify the low energy fluorescent lines the varnish

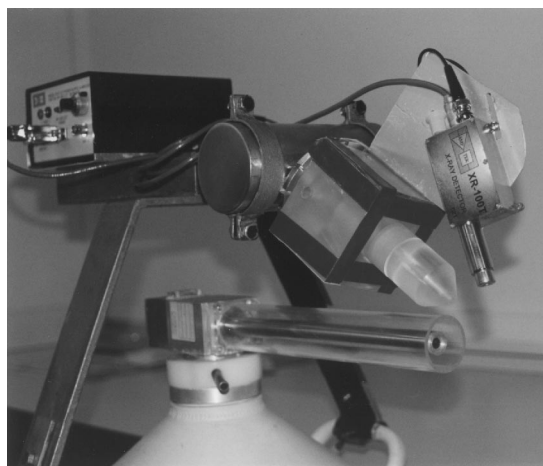


Fig. 1. General view of the portable XRF system used for “in situ” analysis.

layer should be removed from the painting and then we use the Si(Li) detector with a beryllium entrance window of only 8 μm . Once the points of interest on the painting have been selected, the analyses are made with different X-ray tube voltages depending on the elements that integrate the yellow pigments (lead and lead–tin oxides) and the ochre pigments (arsenic sulfides and hydrated iron oxides). A voltage of 35 kV gives us good yield for the line K_{α} of the tin, voltages of 25 and 15 kV give us high yield for L lines of the lead and K lines of the arsenic and iron, and a voltage of 8 kV has been used to excite the L lines of the tin.

3. Results and discussion

A total of 19 altarpieces were analyzed with the equipment previously described. The analyses of the XRF spectra enables identification of the energy and the intensity of the peaks. The selection of the voltage of the X-ray tube is a commitment between the penetration and the electronic transitions that we want to induce on the pigment. We

have used voltages of 8 and 15 kV to excite low energy electronic transitions and to analyze the superficial layers, voltages of 25, and 35 kV have been used to excite higher energy electronic transitions which penetrate more deeply.

The energy and intensity of the XRF spectra are in accordance with the element and its abundance in the painting. However, due to the non-homogeneous distribution of the elements in the matrix of the painting, quantitative analyses have been excluded and only qualitative analysis and a semi-quantitative approximation were estimated. The results from the XRF spectra are expressed in peak-area ratios of those identified elements in relation to the dominant element [4]. The element with the greatest peak-area is classified as dominant; the majority elements are those whose peak-area ratios are up to 10% of the dominant one; and the minority elements are those whose peak-area ratios are lower than 10%. For this classification we have considered only the most intense X-ray lines of the selected elements [7].

Tin has been detected in a total of 11 altarpieces shown in Table 1, the identification has been

Table 1

Occurrences of the lead–tin yellow. The XRF spectra were registered with a X-ray tube potential of 35 kV. (DE: dominant element; ME: majority element; mE: minority element)

Title of picture	Point	Detector	kV	DE	ME	mE
The Holy Cross (Alcañiz, 1410)	Cloak	CZT	35	Pb		Fe _{1:20} , Sn _{1:100} ^{a1}
Presentation of the Child in the temple (Llanos & Yáñez, 1507–10)	Detail in dress	Si(Li)	35	Pb	Fe _{1:7} , Sn _{1:7}	Sr _{1:18} , Hg _{1:20} , Cu _{1:34}
The Adoration of the shepherds (Llanos & Yáñez, 1507–10)	Detail in dress	Si(Li)	35	Pb	Cu _{1:2} , Sn _{1:8}	Au _{1:14}
The Adoration of the Magi (Llanos & Yáñez, 1507–10)	Stocking	Si(Li)	35	Pb	Cu _{1:3}	Sn _{1:16} , Fe _{1:17} , Hg _{1:18}
The Ascension (Llanos & Yáñez, 1507–10)	Dress	CZT	35	Pb	Sn _{1:10}	Cu _{1:23}
St. Ana, The Virgin and The Child with Maria Magdalene. (Macip, 1506)	Blond hair	CZT	35	Pb	Sn _{1:8}	Ni _{1:14}
Predela of the Saints (Macip, 1506)	Palm	CZT	35	Pb	Sn _{1:9}	Ni _{1:40}
St. Denis and St. Margaret (Macip, 1510)	Blond hair	CZT	35	Pb	Sn _{1:4}	Ni _{1:14} , Fe _{1:29}
	Short	CZT	35	Pb		Sn _{1:14} , Ni _{1:18}
The Burial of Christ (Macip, 1529–32)	Skirt of man	CZT	35	Pb	Cu _{1:5} , Sn _{1:8}	
	Sleeve of woman	CZT	35	Pb		Sn _{1:17} , Ni _{1:30}
The Baptism of Christ (Macip, 1535)	Flower	CZT	35	Pb		Sn _{1:14} , Cu _{1:29} , Ni _{1:33}
The Adoration of the Magi (Macip, 1543)	King tunic	CZT	35	Pb	Sn _{1:10}	Ni _{1:26}

^{a1} : x is the ratio between the net area of the XRF peak of an element and the dominant element.

carried out from electronic transitions of the tin lines $K_{\alpha 12}$ (25.154 keV) and $L_{\alpha 12}$ (3.442 keV). As a representative example Fig. 2 shows a spectrum that corresponds to a yellow pigment of the altarpiece titled “The Adoration of the Magi” (Macip, 1543) obtained with a voltage of 35 kV and the detector of CdZnTe, where the $K_{\alpha 12}$ lines of the tin are clearly appreciable jointly the L_{β} lines of the lead. Fig. 2 shows also a detail of the XRF spectra of a yellow pigment from the work “Presentation of The Child in the Temple” (Llanos and Yáñez, 1507) obtained with a voltage of 8 kV and detected by the Si(Li) detector; we can appreciate the $L_{\alpha 12}$ line of the tin that overlap the $K_{\alpha 12}$ (3.312 keV) line of the potassium. The presence of tin and lead in these altarpieces led us to classify the yellow pigment used by the authors as lead-tin yellow. The high intensity of the lines of lead could be due to the use lead-white on the preparation of the wood support or in mixtures with the yellow pigment to soften it.

In the rest of the works shown in Table 2 there are no data that confirm the presence of tin in the yellow pigments. Table 2 shows the occurrences of yellow ochre with the iron as the majority element

and the occurrences of degraded ochre with arsenic as the majority element. In the first case the most intense line of the XRF spectra corresponds to the $K_{\alpha 12}$ transition of the iron and is probably ochre yellow (hydrated iron oxide). In the second case, the arsenic has been identified in the XRF spectra of ochre pigments with orange tonalities that were in a degraded state. These pigments could be arsenic sulfides like the orpiment or realgar due to their tendency to change in mixtures with other pigments [6]. Fig. 3 shows the XRF spectrum of a ochre pigment containing arsenic that correspond to the painting “The Adoration of the shepherds” (Macip, 1529). In this spectrum, obtained with a voltage of 25 kV and the Si(Li) detector, we can see the line $K_{\beta 13}$ (11.722 keV) of the arsenic while its most intense line, $K_{\alpha 12}$ (10.530 keV), coincides with the $L_{\alpha 12}$ (10.541 keV) line of the lead. In this case semi-quantitative analysis have been made using the $K_{\beta 13}$ line of the arsenic and the $L_{\beta 12}$ line of the lead. In the spectra of Fig. 3 we can also observe the presence of iron, copper and mercury that probably proceed from neighboring areas that have been excited simultaneously.

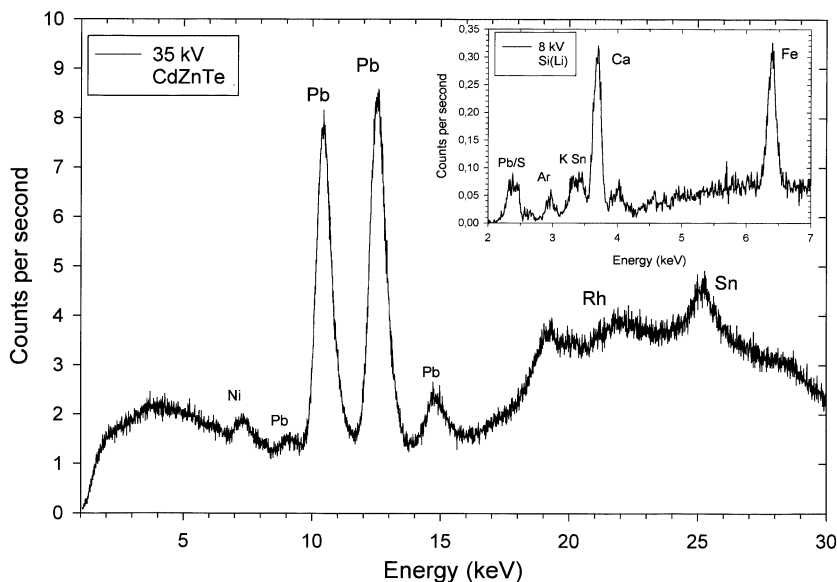


Fig. 2. XRF spectrum, obtained with a voltage of 35 kV and the CdZnTe detector, of a lead–tin yellow pigment from the painting “The Adoration of the Magi” (Macip, 1543). In the upper part we show a detail of the spectrum from the painting “The presentation of The Child in the Temple” (Yáñez and Llanos, 1507) obtained with a voltage of 8 kV and the detector of Si(Li). In both spectra we can see the fluorescence lines of the tin.

Table 2

Occurrences of yellow and ochre pigments. The arsenic is present in degraded ochre pigments. The XRF spectra were registered with a X-ray tube potential of 25 or 15 kV (DE: dominant element; ME: majority element; mE: minority element)

Title of picture	Point	Detector	kV	DE	ME	mE
Presentation of the Virgin in the temple (Llanos & Yáñez, 1507–10)	Blond hair	Si(Li)	15	Fe	Pb _{1:2} , Ca _{1:9} , S _{1:9}	
Visitation of the Virgin to St. Isabel (Llanos & Yáñez, 1507–10)	Skirt	Si(Li)	15	Fe	Ca _{1:3}	As _{1:18}
The hug in the golden door (Llanos & Yáñez, 1507)	Basket	Si(Li)	15	Pb	Fe _{1:2} , S _{1:6} , Cu _{1:9}	Ca _{1:18}
The Holy Cross (Alcañiz, 1410)	Robe	Si(Li)	25	Pb	Fe _{1:3}	Ca _{1:22} , Zn _{1:50} , Cu _{1:64}
The Burial of christ (Macip, 1529–32)	Sleeve	CZT	25	Pb	Fe _{1:5}	Ca _{1:98}
Fall of Saulo (Macip, 1545)	Soldier	CZT	25	Pb	Fe _{1:10}	Cu _{1:23} , Sr _{1:37} , Ca _{1:53}
The mystic weddings of the venerable Agnesio (Juanes, 1553–58)	Sleeve of Inés	CZT	25	Pb		Cu _{1:19} , Fe _{1:70}
Nativity of Maria (Llanos & Yáñez, 1507–10)	Bodice	Si(Li)	25	Pb		Fe _{1:30} , Cu _{1:30}
The Adoration of the shepherds (Macip, 1529–32)	Tunic	Si(Li)	25	Pb	As _{1:2} , Fe _{1:4} , Cu _{1:4} , Ca _{1:6}	Hg _{1:26}
	Sleeve	Si(Li)	25	Pb	As _{1:2} , Ca _{1:4} , Fe _{1:5}	Cu _{1:10} , Hg _{1:26}
Chirst tied to the Column (Macip, 1535)	column	CZT	25	Pb	Fe _{1:4} , As _{1:7}	Ca _{1:33}

^{a1} : x is the ratio between the net area of the XRF peak of an element and the dominant element.

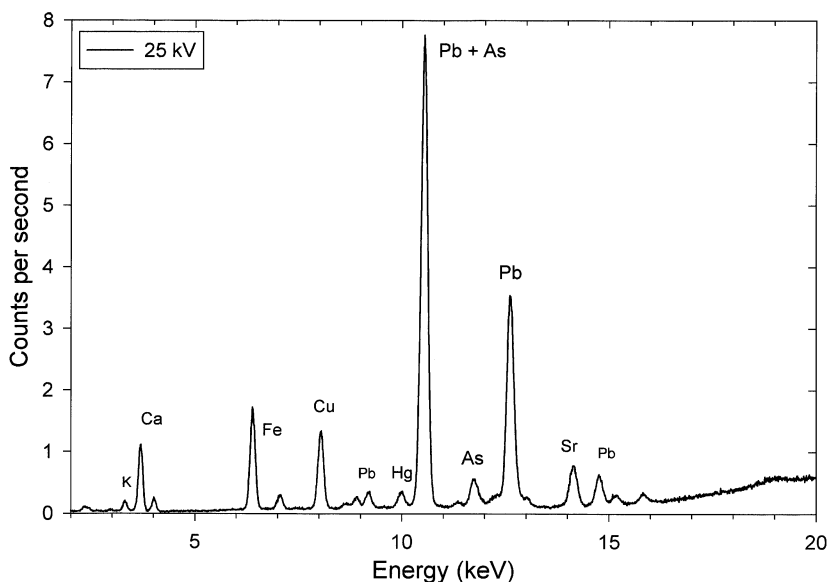


Fig. 3. XRF spectrum, obtained with a voltage of 25 kV of an ochre pigment composed of arsenic from the painting “The Adoration of the shepherds” (Macip, 1529). The spectrum has been detected with the Si(Li) detector. The $K_{\alpha 12}$ (10.530 keV) line of the arsenic is overlapped by the $L_{\alpha 12}$ (10.541 keV) line of the lead.

The peculiarity in Tables 1 and 2 that the lead is the dominant element is due to the use of the lead-white in the last layer of the preparation of the support and in the mixtures to obtain different chromatic tonalities.

4. Conclusions

The Archaeometry Unit of the ICMUV has configured a portable XRF equipment that enabled us to carry out qualitative and non-destructive “in situ” analyses to study medieval paintings from the Museo de Bellas Artes of Valencia. The XRF system is integrated by a X-ray tube (0–50 kV, 1 mA), a high resolution cryogenic Si(Li) detector and a small size Peltier cooled CdZnTe.

With this XRF system we have analyzed altarpieces by M. Alcañiz, V. Macip, H. Llanos, H. Yáñez and J. de Juanes, painters that developed their artistic work in Valencia during the XV and XVI centuries. We have identified lead–tin yellow in several of their analyzed works. The use of this yellow pigment reveals influences from the European schools that used it from the XIII century [5] and that probably was introduced in Valencia by artists formed in the Italian schools. Together with the lead-tin yellow other yellow pigments have been identified and are composed by iron. Degraded ochre pigments analyzed in the paintings are composed by arsenic.

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