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3 1 **CHARACTERIZATION OF “OIL ON COPPER” PAINTINGS BY ENERGY DISPERSIVE X-**  
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5 2 **RAY FLUORESCENCE SPECTROMETRY**  
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9 4 A. Pitarch<sup>1</sup>, A. Ramón<sup>2</sup>, A. Álvarez-Pérez<sup>3</sup>, I. Queralt<sup>1</sup>

10  
11 5 <sup>1</sup>Laboratory of X-ray Analytical Applications, Institute of Earth Sciences “Jaume Almera”, CSIC, Solé  
12  
13 6 Sabarís Street, 08028 Barcelona, Spain.

14  
15 7 <sup>2</sup>1926' AR Art Gallery, Palla Street 25, 08002 Barcelona, Spain.

16  
17 8 <sup>3</sup>Department of Geology, Faculty of Sciences, Autonomous University of Barcelona, 08193 Bellaterra,  
18  
19 9 Barceloma, Spain.

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23 11 **Abstract**

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25 12 Energy dispersive X-ray fluorescence is a common analytical tool for layer thickness measurements in  
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27 13 quality control processes in coating industry, but there are scarce microanalytical applications in order to  
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29 14 ascertain semi-quantitative or quantitative information of painted layers. “Oil on copper” painting  
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31 15 becomes a suitable material to be analysed by means of X-ray fluorescence spectrometry, due to the  
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33 16 metallic nature of substrate and the possibility to apply layered models as used in coating industry. The  
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35 17 aim of this work is to study the suitability of a quantitative EDXRF methodology for the assessment of  
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37 18 the areal distribution of pigments and the characterization of painting methods on such kind of pictorial  
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39 19 artworks. The method was tested on standard reference materials: dried droplets of monoelemental  
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41 20 standard solutions laid on a metallic plate of copper. As an example of application, we estimated pigment  
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43 21 mass distribution of two “oil on copper” painting from the sixteenth and eighteenth century respectively.  
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45 22 Pictorial layers have been complementarily analyzed by X-ray diffraction.

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47 23 Apart of the supporting media made of copper or brass, we could identify two different superimposed  
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49 24 layers: a) a preparation layer mainly composed by white lead and b) the pictorial layer of variable  
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51 25 composition depending on the pigments used by the artist on small areas of the painting surface. The areal  
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53 26 mass distribution of the different elements identified in the painting pigments (Ca, Cr, Mn, Fe, Zn, Cd,  
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55 27 Hg and Pb) have been determined by elemental mapping of some parts of the artworks.

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57 28  
58 29 *Keywords:* non destructive analysis; EDXRF; pigment mass distribution; “oil on copper”.  
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1  
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3 31 Corresponding author:  
4  
5  
6 32

7 33 Africa Pitarch Martí

8  
9 34 Laboratory of X-ray Analytical Applications

10 35 Institute of Earth Sciences "Jaume Almera" – ICTJA

11 36 Spanish Council for Scientific Research - CSIC

12  
13 37 Solé Sabarís Street s/n

14 38 08028 Barcelona - Spain

15  
16 39 E-mail address: [apitarch@ija.csic.es](mailto:apitarch@ija.csic.es)

17 40 Telephone: +34 93 409 54 10

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19 41 Fax: +34 93 411 00 12  
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## 1. Introduction

The practice of painting in oil on a copper support has its origins in the sixteenth century in Italy and was widespread in the rest of Europe during the seventeenth century. The artists painted portraits, landscapes and religious subjects on small sheets of copper or brass (often old printmaking plates) to decorate objects such as furniture or dresses. The painting technique had diverse stages; once the artist had obtained his copper plate, it required roughening prior to painting. Then, a priming coat (typically a thin layer of white lead and umber in oil) was laid down to also help the paint adhere [1]. This practice remained till the end of the nineteenth century, when lead grounds began to be substituted by zinc white grounds [2].

It is well known that Energy Dispersive X-ray fluorescence (EDXRF) is a common analytical tool for layer thickness measurements in many classical industrial applications, such as quality control processes in coating industry [3]. In the area of Cultural Heritage analyses EDXRF has become a powerful tool towards the obtaining of qualitative information about the chemical composition of inorganic pigments [4-8]. Moreover, recent studies reported that EDXRF spectrometry in combination with other techniques such as visible reflectance spectrometry (vis-RS) or even alone can be successfully applied, in a wide range of cases, to reconstruct stratigraphy and thickness of paint layers or even in photograph films [9-15]. In the particular area of quantitative analysis of multilayered paintings, there had been published some works [16-17], but there are no specific investigations in order to obtain semi-quantitative information of the areal distribution of pigments in a complete non-destructive way. In this way, this kind of artwork becomes a perfect material to be analysed by means X-ray fluorescence spectrometry, due to the metallic nature of the substrate. The aim of this work is to study the suitability of a quantitative EDXRF method designed specifically for the approximation of pigment mass distribution on "oil on copper" multilayer paintings.

## 2. Materials and methods

### 2.1. Artworks

Two "oil on copper" paintings from presumable different ages were selected for this study. Both of them belong to the private collection of 1926' AR Art Gallery (Barcelona, Spain). The first one represents a scene of a Franciscan habit Saint holding a wooden cross in his outstretched arms. The accuracy of the

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72 stroke and the employed colours (its palette is composed by green, golden, red, skin-coloured and brown  
73 in different tonalities) suggest that this is an Italian work made in the second half of the sixteenth century  
74 (**Fig. 1**). The second painting under study represents a river landscape scene. Although the painting it is in  
75 bad state of conservation (it has micro cracks in excess, probably due to the poor preparation of the  
76 copper plate) the colours are still very vivid (its palette is composed by white, yellow, pink, orange, deep  
77 red, brown, green and blue). Such kind of detailed scenes were in vogue during the eighteenth century,  
78 especially in the bourgeois Dutch market (**Fig. 2**).

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80 The major requirement for this analytical study was the ability to perform non-destructive measurements,  
81 due to the historical value of both artworks. In a first stage, then, the “oil on copper” paintings were  
82 examined using non-destructive EDXRF to qualitatively determine the elemental composition of  
83 pigments present in the paintings. In addition, X-ray Diffraction (XRD) was also employed not only to  
84 reach information on the compositional properties of the painting by crystalline phase analysis but also to  
85 characterize the nature of the different layers for the proper development of the EDXRF layer model.

## 86 87 *2.2. XRD instrumentation*

88 The diffractometer used for the study of the artworks was a D8 Advance (Bruker AXS GmbH, Germany)  
89 instrument with a Cu K $\alpha$  target tube X-ray source (operating at 40 kV and 40 mA), a primary Göbbel  
90 mirror and an energy dispersive SOL-X detector. The samples were mounted on a mobile plate stage to  
91 adequately align the system, so that measurements were carried out in a completely non-destructive way,  
92 without previously preparing or adapting the sample for the analyses on the conventional sample holders.  
93 The angular range ( $2\theta$ ) was explored by a goniometer scanning from 4° to 60°, at a step size of 0.05° and  
94 a counting time of 3 seconds per step. Evaluation of X-ray diffractograms was performed by using the  
95 routines of the Diffrac.Suite™ software package (Bruker AXS GmbH, Germany) and the attached  
96 specific powder diffraction file (PDF) database (International Centre for Diffraction Data - ICDD,  
97 Pennsylvania, USA).

## 98 99 *2.3. EDXRF equipment*

100 We used a bench top small-spot energy dispersive X-ray fluorescence spectrometer (XDV-SD® model,  
101 Helmut Fischer GmbH, Germany) designed for coating –thickness measurement and materials testing. It

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4 102 consists on a microfocus tungsten anode X-ray tube (using a maximum power of 50 W, a maximum  
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6 103 voltage of 50 kV and a maximum current of 1 mA) and a Si-Pin semiconductor detector (Peltier cooling  
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8 104 at -50°C; with 180 eV FWHM at Mn K $\alpha$ ). The spectrometer is equipped with 5 primary filters (nickel  
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10 105 10 $\mu$ m, molybdenum 70  $\mu$ m, aluminium 500  $\mu$ m and 1000  $\mu$ m and titanium 300  $\mu$ m) and four collimators  
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12 106 (0.1, 0.3, 1 and 3 mm in diameter). A video camera allows viewing and selection of the irradiated area  
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14 107 with up to  $\times 45$  magnification and the motorized X-Y-Z stage allows focusing and searching of the points  
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16 108 of interest. The instrument can be used to obtain elemental chemical mappings by programming a grid of  
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18 109 points for analysis.  
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#### 21 111 2.4. Standards for EDXRF calibration

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23 112 After the screening phase analysis carried out on the artworks, nine elements were selected for the  
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25 113 preparation of a standard set used to calibrate the EDXRF instrument for the analysis of “oil on copper”  
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27 114 paintings. Elemental stock solutions (TraceCERT®, Fluka, Sigma Aldrich Chemie, GmbH, Germany;  
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29 115 1000mg/L) of calcium, chromium, manganese, iron, zinc, cadmium, gold, mercury and lead were used for  
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31 116 this purpose, following similar procedures than those reported by *Fittschen and Havrilla* [18] but at  
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33 117 different scale. An aliquot of 1 $\mu$ L of each solution was transferred onto a copper support by using a  
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35 118 micro-syringe (7000 Series Modified Microliter™, Hamilton, USA) and left to dry at room temperature  
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37 119 before EDXRF analysis. We obtained some small dried residues, each one containing 1 microgram of the  
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39 120 different considered elements. These dried residues have an approximate diameter around 600 microns.  
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#### 42 122 2.5. EDXRF quantitative method

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44 123 A methodology for analysis of “oil on copper” multilayered paintings was developed by using the  
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46 124 WinFTM® Software Program version 6.20 (Helmut Fischer GmbH + Co. KG, Germany). This software  
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48 125 program uses the fundamentals described in [19-20] for the evaluation of the measured spectrum and  
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50 126 allows designing different layered models (single, double, multilayers) taking into account the main  
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52 127 features of the layers and substrates. Amongst the possibilities and variables needed to define a method  
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54 128 for the measuring layer, the program allows introducing the following spectral data: a) spectra of  
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56 129 material's base of standards (a copper support in this case); b) spectra of the standards used for the  
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58 130 calibration (monoelemental solutions) and c) spectra of the material's base of the samples to be analysed.  
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60 131 This last point was fulfilled by the analysis of the backside of the “oil and copper” paintings.

Looking for the best conditions for analysis of the previously prepared standard set, different conditions (filter, collimator, voltage and current) were checked. We used an aluminium filter of 1000  $\mu\text{m}$  in thickness (in order to reduce the background noise from tungsten tube at the region of interest in the spectrum) and the collimator of 1 mm in diameter (in order to adjust the X-ray focal spot for the irradiation of the whole dried droplet surface of calibration dataset). The spectra acquisition time was optimised to ensure that counting statistics is good enough to guarantee the quality of analytical results. We choose 50 kV and 1000  $\mu\text{A}$  as voltage excitation and anode current respectively, taking into consideration the counting rates. To obtain the minor relative standard deviation (RSD), repeated measurements were carried out (on the same point and using the same analytical conditions, 6 analyses at different measuring times: 50, 100, 300, 500, 1000 s). A measuring time of 300 s delivers an approximately RSD of 1% whilst a more extended time does not imply a significant reduction in the RSD value (**Fig. 3**). Then we select this counting time as the best for spectra obtaining at our instrumental design.

The detection limit ( $DL$ ) obtained by EDXRF were calculated according to the equation:

$$DL = 3 \frac{C_i \sqrt{N_b}}{N_p}$$

where:  $C_i$  is the concentration of the element  $i$ ;  $N_b$  is the net peak area of the background and  $N_p$  is the net peak area of the analytical line of the element  $i$ . The results for the standard set are presented in Table 1.

Once the methodology for routine analysis of “oil on copper” multilayered paintings was tuned up, and taking into consideration the particular features of both artworks, measurements were carried out by using a voltage excitation of 50 kV, an anode current of 1000  $\mu\text{A}$ , an aluminium filter of 1000  $\mu\text{m}$  in thickness, a spectrum measuring time of 300 s and a focal spot of 1 mm in diameter. Chemical mappings were also carried out in order to observe the distribution of elements along selected areas of the paintings. Measuring conditions were the same ones as the defined for punctual analyses with exception of the counting time, which was reduced to 60 s per each point due to the large number of measurements to be done. In some cases we analysed some artwork details smaller than 1mm by using the 0.3 mm collimator mask then determining the elemental concentration by the areal ratio of both focal spots (1 and 0.3 mm).

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161 *2.6. Statistical data treatment*

162 Once we quantified the elements from both artworks, we tried to identify clustering concerning the  
163 different colouration by using Principal Component Analysis (PCA). The main objective of PCA is to  
164 simplify the study of complex data systems by identifying a relative small number of components that can  
165 be used to represent relationships amongst groups of many interrelated discrete variables, in this case the  
166 features of both studied artworks. Statistical analysis was performed with the software package  
167 STATISTICA 7.0.

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169 **3. Results and discussion**

170 *3.1. Elemental and crystalline phase analyses of the supporting materials and preparation layers.*

171 Analysis of the supporting material was made by obtaining an EDXRF spectrum from the backside of  
172 each plate, in which we only can distinguish the signal from copper and minor titanium, iron and lead  
173 impurities at trace level, thus deducing the use of pure copper plate as a supporting material of the  
174 Franciscan Saint painting (**Fig. 4a**). The river landscape painting exhibit copper and zinc as a major  
175 elements, joined by titanium, iron and lead impurities at trace level, thus deducing the use of zinc-bearing  
176 brass plate as a supporting material (**Fig. 4b**). XRD spectral data of the painting side supported these  
177 results, revealing the presence of the characteristic peaks a copper based alloy (**Fig. 5a**, see peaks labelled  
178 as #) and brass (**Fig. 5b**, see peaks labelled as  $\beta$ ).

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180 The omnipresence of lead all over the painting showed an important role of some lead compound, so that  
181 it was investigated by X-ray diffraction. As it was previously mentioned, the painting technique on such  
182 kind of supports was usually based on laying down one white lead thin layer to promote enough  
183 roughness to help oil paint adhere [1]. XRD experimental data confirmed the presence of hydrocerussite  
184 (**Fig. 5a**, see peaks labelled as \*) which is a lead carbonate hydroxide mineral with the composition  
185  $(\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2)$  and cerussite ( $\text{PbCO}_3$ ) (**Fig. 5b**, see peaks labelled as &). These terms should  
186 properly refer to the natural mineral forms, so further on we will refer to the pigment as lead white.  
187 Although the artificial form was synthesised since ancient times, the fact that we only identified lead  
188 white in the preparation layer would confirm that both artworks were surely done before the nineteenth  
189 century.

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191 3.2. Pigment mass distribution estimation on a Renaissance painting

192 As revealed by the spectral data obtained by EDXRF analyses we can distinguish the presence of calcium,  
193 manganese, iron, copper, gold, mercury and lead.

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195 Copper signal is present in all the spectra and it can appear as a result of the emission of copper from  
196 support and by its potential presence in the pigments of green colouration. However, as we cannot clearly  
197 differentiate by EDXRF experimental data the origin of the copper signal in the spectra, the estimated  
198 areal concentration cannot be distinguished. Nevertheless, the contribution from the support is clearly  
199 ascertained from the attenuation of Cu K $\alpha$  line intensity in the carnations, due to the strong lead-bearing  
200 pigment absorption. Despite the fact that the contribution of copper based pigments cannot be  
201 distinguished by EDXRF analysis, XRD experimental data (**Fig. 5a**) confirmed the presence of basic  
202 copper sulphates such as brochantite (Cu<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>6</sub>) and posnjakite (Cu<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>6</sub>·H<sub>2</sub>O). The first  
203 mention of the use of these pigments dates back to the seventeenth century [21].

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205 The main results relating to the elemental chemistry of the Renaissance painting are summarized in **Table**  
206 **2**. The relationship between colouration and chemical data can be deduced from the elemental surface  
207 distribution reported in **Fig. 6**. Calcium is concentrated around the Saint's face and the wooden cross.  
208 Intense brownish colours exhibit the highest contents of iron (711  $\mu\text{g}/\text{cm}^2$ ) and major presence of  
209 manganese (38.2  $\mu\text{g}/\text{cm}^2$ ). Lead is widely distributed all over the piece, although the amount of lead is  
210 several times higher in the carnations (7539  $\mu\text{g}/\text{cm}^2$ ) indicating their additional use for the base pigment at  
211 these parts. Reddish parts of the picture (lips, eyebrows and carnations) exhibit the presence of mercury  
212 being the highest one in the Saint's lips (572  $\mu\text{g}/\text{cm}^2$ ). Gold is restricted to golden crown (585  $\mu\text{g}/\text{cm}^2$ ).

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214 For the proper interpretation of the whole dataset, a PCA routine was carried out. Gold (Au) was not  
215 taken into account since it is only characteristic of the golden crown. By comparing the compositional  
216 pattern (the selected variables were Ca, Mn, Fe, Hg and Pb) the principal component analyses allowed us  
217 to differentiate colours according to their elemental content. The extraction of two factors implies the  
218 68% of the explained variance. Factor 1, explaining the 47% of the total variance, has positive high loads  
219 for Mn and iron while Factor 2, which explains the 21% of the total variance, has a strong negative load  
220 for Hg. As shown in **Fig. 7**, which illustrates the position of different cases respect to the two main



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3 221 factors, 3 main groups can be observed. The first group (**Fig. 7a**) is composed by red tonalities (lips and  
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5 222 skin-coloured carnations); brownish shades (light and dark brown from clothes and orangey brown from  
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7 223 the cross) compound the second group (**Fig. 7b**) while the third one is composed by green and golden  
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9 224 colours (**Fig. 7c**).  
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### 12 226 *3.2.3. Pigment mass distribution estimation on a Contemporary painting*

13 227 As revealed by the spectral data obtained by EDXRF analyses we can observe the presence of Ca, Mn,  
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15 228 Cr, Fe, Cu, Zn, Cd and Pb.  
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19 230 Zinc signal is present in all the spectra and it can appear as a result of the emission of zinc-bearing brass  
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21 231 from support and also by its potential presence in the pigments. As it has happened with copper in the  
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23 232 Renaissance portrait, we cannot clearly differentiate by EDXRF analysis whether the potential  
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25 233 contribution of the zinc signal in the spectra is related to the pictorial layer, the supporting base or from  
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27 234 both of them; however, by using XRD analysis the presence of zincite (ZnO) was recorded (**Fig. 8**). The  
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29 235 presence of this compound revealed the use of modern pigments such as zinc white, which is not typical  
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31 236 in paintings before the middle of the nineteenth century.  
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35 238 The main results relating to the elemental chemistry of the Contemporary painting are summarized in  
36  
37 239 **Table 3**. The relationship between colouration and chemical data can be deduced from the elemental  
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39 240 surface distribution illustrated in **Fig. 9**. Calcium and lead are distributed all over the piece. Highest  
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41 241 contents are found on the white shades but also in other colours, what suggest that they were probably  
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43 242 used as a pigmenting supports. (Ca: 2258  $\mu\text{g}/\text{cm}^2$ , Pb: 14416  $\mu\text{g}/\text{cm}^2$ ). Cadmium is restricted to pinkish  
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45 243 and orangey colours (704  $\mu\text{g}/\text{cm}^2$  and 305  $\mu\text{g}/\text{cm}^2$  respectively). The highest contents of iron are recorded  
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47 244 in the green flag, although the brownish parts of the picture also show iron in relevant amount (445  
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49 245  $\mu\text{g}/\text{cm}^2$  and 189  $\mu\text{g}/\text{cm}^2$  respectively). The presence of manganese is restricted to warm colours (pink,  
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51 246 orange and brown) and its content is often at trace level. Chromium is mainly distributed in both the  
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53 247 bluish and yellowish shades of the sky and the water (being the highest contents 1567  $\mu\text{g}/\text{cm}^2$  for the sky  
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55 248 and 180  $\mu\text{g}/\text{cm}^2$  for water).  
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4 250 Statistical routine was also performed to the obtained semi-quantitative data from this artwork. The first  
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6 251 two factors found for the River landscape “oil on copper” painting explain the 71% of the variability of  
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8 252 the system. Factor 1, which explains the 38.86% of the total variance, has high positive load for Ca and  
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10 253 negative load is for Fe. Factor 2, explaining the 32.26% of the total variance, has high positive loads for  
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12 254 Pb while a high negative load of this factor for Cr. In **Fig. 10**, which represents the position of the  
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14 255 different cases respect to the two main factors, we broadly distinguish 3 main clusters: clusters  
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16 256 corresponding to warm tonalities and the green colour are found approximately in the same region of the  
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18 257 scatter plot and constitute the first cluster (**Fig. 10a**); the second one is constituted by bluish and yellow  
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20 258 tonalities from both the sky and the water (**Fig. 10b**) and the third cluster is composed by white colour  
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22 259 (**Fig. 10c**).  
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#### 25 261 **4. Conclusions**

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27 262 Two “oil on copper” paintings, from presumable different ages, were investigated and characterized by  
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29 263 X-ray spectroscopy (X-ray diffraction and energy dispersive X-ray fluorescence) revealing differences  
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31 264 not only in the support and in the preparation layers but also in the elemental chemistry of pigments.  
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35 266 In both cases, results of the analyses suggest that there are at least 2 superimposed layers (apart of the  
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37 267 supporting media made of copper or brass): a priming coat mainly composed by lead white and a pictorial  
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39 268 layer of different composition (depending on the area of analysis).  
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43 270 The first painting, attributed to the Renaissance period, is characterized by a copper plate support, a white  
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45 271 lead pictorial base ( $\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ ) and the presence of Ca, Mn, Fe, Cu, Au, Hg and Pb. The second  
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47 272 one, presumably from the second half of the eighteenth century and made over a brass support, is  
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49 273 characterized by a white lead pictorial base ( $\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2$  and  $\text{PbCO}_3$ ) and the presence of Ca, Cr,  
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51 274 Mn, Fe, Cu, Zn, Cd and Pb. The presence of white lead as a preparation layer suggest that both artworks  
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53 275 where conceived before the nineteenth century since it was on that period when the use of white lead was  
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55 276 progressively abandoned due to its high toxicity [2].  
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59 278 The compositional features, revealed by the combined use of XRD and EDXRF, not only suggest that the  
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279 second painting is more recent than the attributed to Renaissance period but also confirm that the second

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3 one (the River Landscape “oil on copper” painting) was in fact carried out at the end of the eighteenth  
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5 281 century (the joint presence of chromium and cadmium was recorded and the presence of zinc white, a  
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7 282 pigment that was commercially available at the end of the eighteenth century [22], were observed). This  
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9 283 chronology is in accordance with the stylistic features described by the art historians.  
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13 285 A simple and rapid method based on non-invasive direct analysis of solid sample was developed for the  
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15 286 determination of pigment mass distribution of “oil on copper” multilayered paintings by using the  
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17 287 WinFTM® Software Program version 6.20 (Helmut Fischer GmbH, Germany). The method is calibrated  
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19 288 by using the dried residues of small droplets of pure elemental solutions, thus obtaining the sensitivity  
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21 289 library for estimations of the areal absolute mass distribution. The program allows the possibility to  
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23 290 compensate spectral differences from different metallic supports used to create these paintings, by  
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25 291 introducing the whole spectrum of standard’s support, and the spectrum of the pictorial support. By  
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27 292 treating the obtained results with the proper statistical routines (such as Principal Component Analyses) it  
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29 293 is possible to find out some differences between colours according to their elemental content.  
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45 301 Autonomous University of Barcelona (UAB).  
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Table 1 Estimated areal detection limits ( $\mu\text{g}\cdot\text{cm}^{-2}$ )

Ca	Cr	Mn	Fe	Zn	Cd	Au	Hg	Pb
14.4	2.6	3.1	2.7	5.9	7.7	5.3	6.9	4.2

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Table 2 Elemental concentration values ( $\mu\text{g}\cdot\text{cm}^{-2}$ ) from different areas of the "oil on copper" portrait

	Ca	Mn	Fe	Au	Hg	Pb
<i>skin coloured</i>						
min	tr	tr	tr	nd	29.9	5814
max	175	tr	38.8	-	157	7539
<i>red</i>						
min	62.0	tr	59.9	nd	229	1093
max	180	6.3	110	-	572	1816
<i>orangey brown cross</i>						
min	50.6	tr	358	nd	0	1835
max	173	14.2	643	-	65.2	3193
<i>green</i>						
min	tr	tr	54.9	nd	nd	827
max	79.1	5.3	112	-	-	1043
<i>dark brown clothes</i>						
min	120.4	12.5	353	nd	tr	829
max	163.3	38.2	711	-	33.2	1598
<i>light brown clothes</i>						
min	104	6.2	91.5	nd	tr	2001
max	182	11.1	111	-	15.4	2638
<i>crown</i>						
min	28.9	tr	62.4	463	11.7	935
max	54.8	3.5	76.1	585	30.9	1023

nd: non detected

tr: traces

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Table 3 Elemental concentration values ( $\mu\text{g}\cdot\text{cm}^{-2}$ ) from different areas of the "oil on copper" river landscape

	Ca	Cr	Mn	Fe	Cd	Pb
<i>Orange man</i>						
min	282	15.0	6.8	215	554	2290
max	792	27.9	28.7	349	703	3782
<i>Orange Boatman</i>						
min	179	23.9	tr	55.3	340	1917
max	473	32.1	9.0	95.1	475	2901
<i>Pink House</i>						
min	341.4	8.1	tr	45.5	248	1748
max	415.4	14.7	3.9	67.0	305	2526
<i>Dark Brown Bridge</i>						
min	70.9	8.5	tr	84.3	0.0	570
max	155	12.9	9.7	188	26.8	754
<i>Green flag</i>						
min	184	7.1	3.7	251	tr	1101
max	421	18.0	10.5	445	50.8	2835
<i>Blue Water</i>						
min	341	45.0	nd	tr	10.9	2015
max	900	180	-	20.5	73.5	4461
<i>Blue Sky</i>						
min	545	52.0	tr	tr	20.3	3220
max	872	87.8	3.7	21.7	74.1	4456
<i>Yellow Sky</i>						
min	192	118	tr	3.2	tr	1523
max	372	157	9.6	20.7	21.3	1941
<i>White Sky</i>						
min	1055	tr	tr	tr	41.6	6909
max	2258	16.8	14.2	33.2	77.5	14416

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nd: non detected

tr: traces

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For Peer Review



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3 1 Figure captions  
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5 2 Fig. 1. Portrait of Saint Bernardino of Siena “oil on copper” painting.  
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7 3 Fig. 2. River landscape “oil on copper” painting.  
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9 4 Fig. 3. Plot of RSD vs. measuring time for Mn. Experimental conditions: 6 measurements on each point,  
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11 5 Al 1000  $\mu\text{m}$  filter, 50 kV, 1000  $\mu\text{A}$ , focal spot 1 mm.  
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13 6 Fig. 4. a) EDXRF spectrum from the backside of the Renaissance painting and b) EDXRF spectrum from  
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15 7 the backside of the Contemporary artwork.  
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17 8 Fig. 5. a) Diffractogram of the Renaissance painting and b) diffractogram of the Contemporary artwork  
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19 9 Key: #: copper alloy; \*: hydrocerussite; +: copper sulphate compound; v: calcite;  $\beta$ : brass (Cu-Zn alloy);  
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21 10 &: cerussite; ^: gypsum;  $\gamma$ : zincite.  
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23 11 Fig. 6. a) Detailed image of the studied area showing the gridding of the X-ray map. Elemental surface  
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25 12 distribution in  $\mu\text{g cm}^{-2}$  of: b) Ca; c) Fe; d) Pb; e) Hg and f) Au.  
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27 13 Fig. 7. Scatter plot of Factor 1 vs. Factor 2 of the analysed areas from the Renaissance painting. Red  
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29 14 colour is represented by black circles; skin colour is shown by black squares; dark brown is represented  
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31 15 by black triangles; orangey-brown is shown by black rhombus; light brown is represented by triangles;  
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33 16 golden is represented by stars and green colour is shown by circles.  
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35 17 Fig. 8. Diffractograms of the Contemporary artwork obtained in different areas: i) blue water; ii) blue sky.  
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37 18 Key: \*: hydrocerussite; v: calcite;  $\beta$ : brass (Cu-Zn alloy);  $\gamma$ : zincite.  
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39 19 Fig. 9. a) Detailed image of the studied area from the Contemporary painting illustrating the gridding of  
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41 20 the X-ray map. Elemental surface distribution in  $\mu\text{g cm}^{-2}$  of: b) Ca; c) Cr; d) Fe; e) Cd and f) Pb.  
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43 21 Fig. 10. Scatter plot of Factor 1 vs. Factor 2 of the analysed areas from the Contemporary painting.  
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45 22 Orange colour from the man is represented by black circles; orange colour from the boatman is shown by  
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47 23 circles; brown colour is shown by black squares; yellow is represented by black triangles; blue from the  
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49 24 sky is shown by black rhombus; the blue from the water is represented by rhombus; green is shown by  
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51 25 triangles; white is represented by stars and pink colour is shown by squares.  
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Figure 1  
61x90mm (600 x 600 DPI)

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Figure 2  
124x108mm (600 x 600 DPI)

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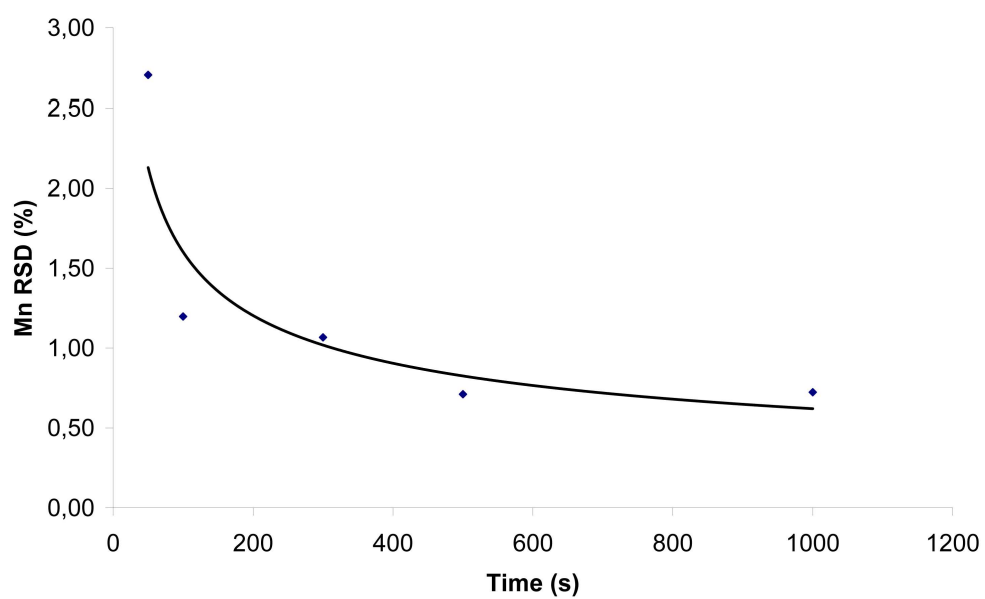


Figure 3  
253x156mm (300 x 300 DPI)

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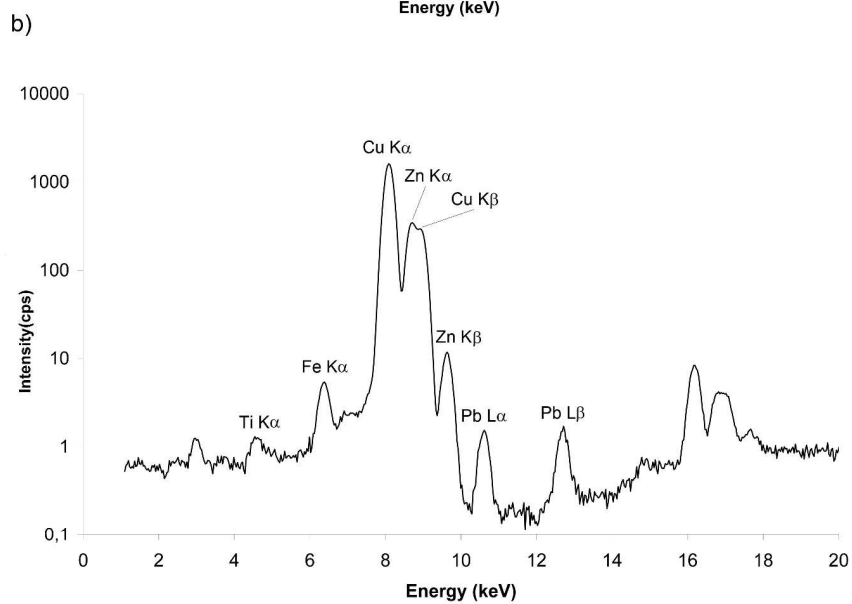
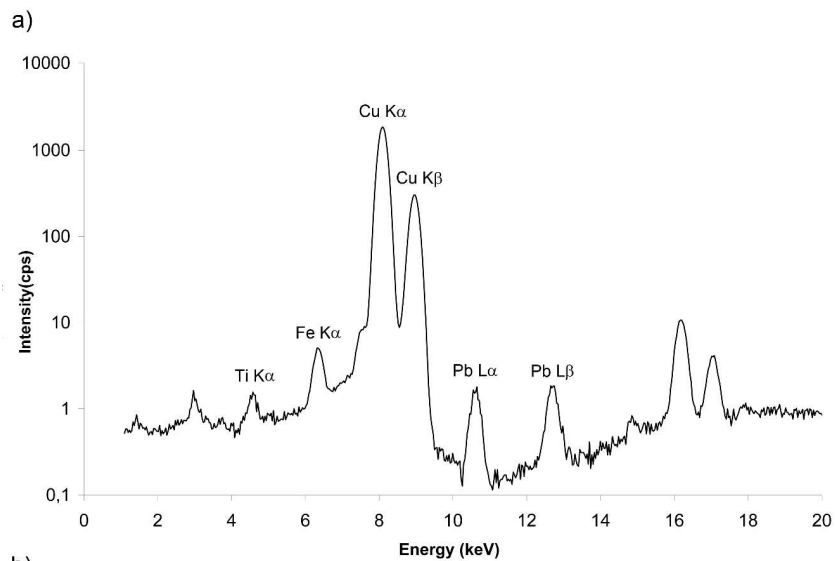


Figure 4  
235x320mm (300 x 300 DPI)

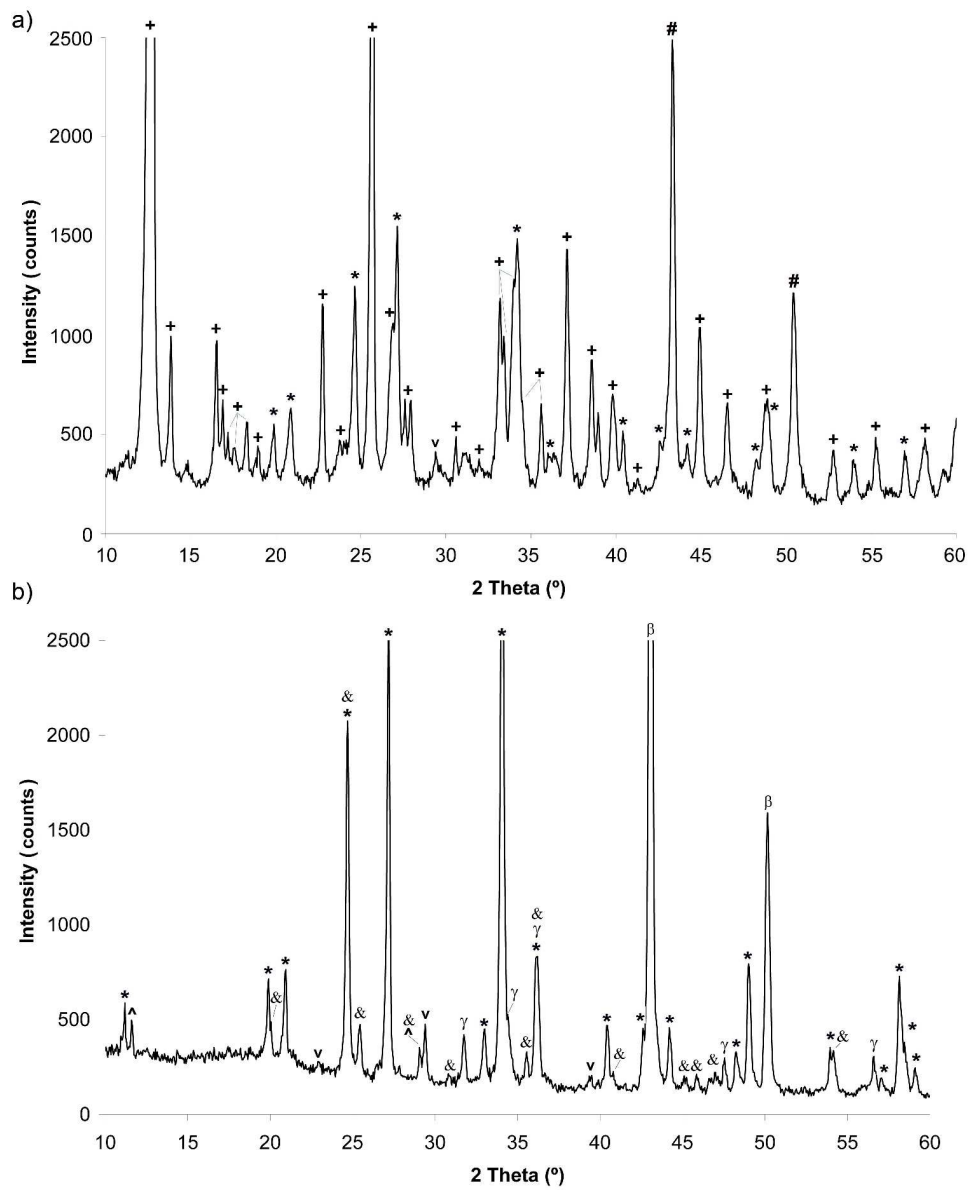


Figure 5  
259x320mm (300 x 300 DPI)

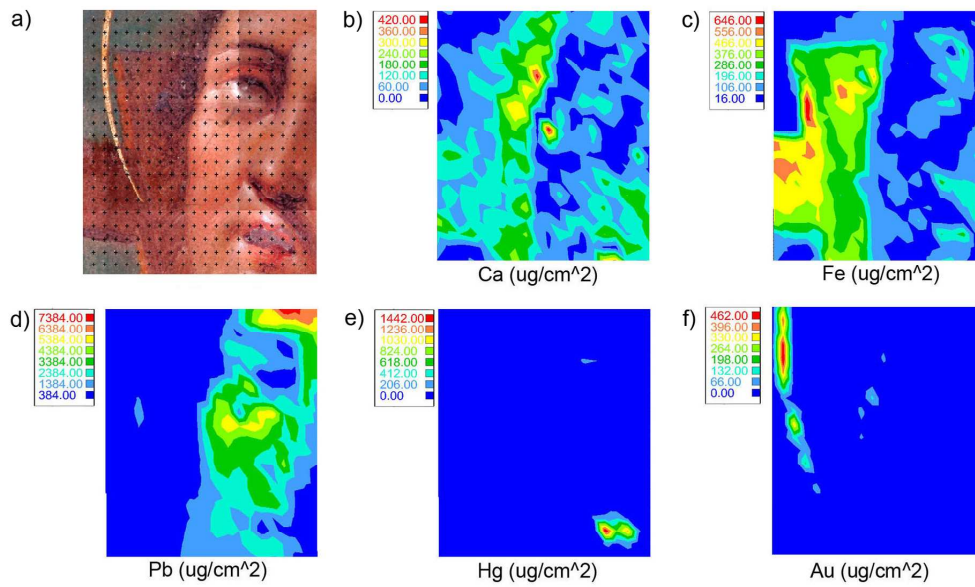


Figure 6  
157x95mm (600 x 600 DPI)

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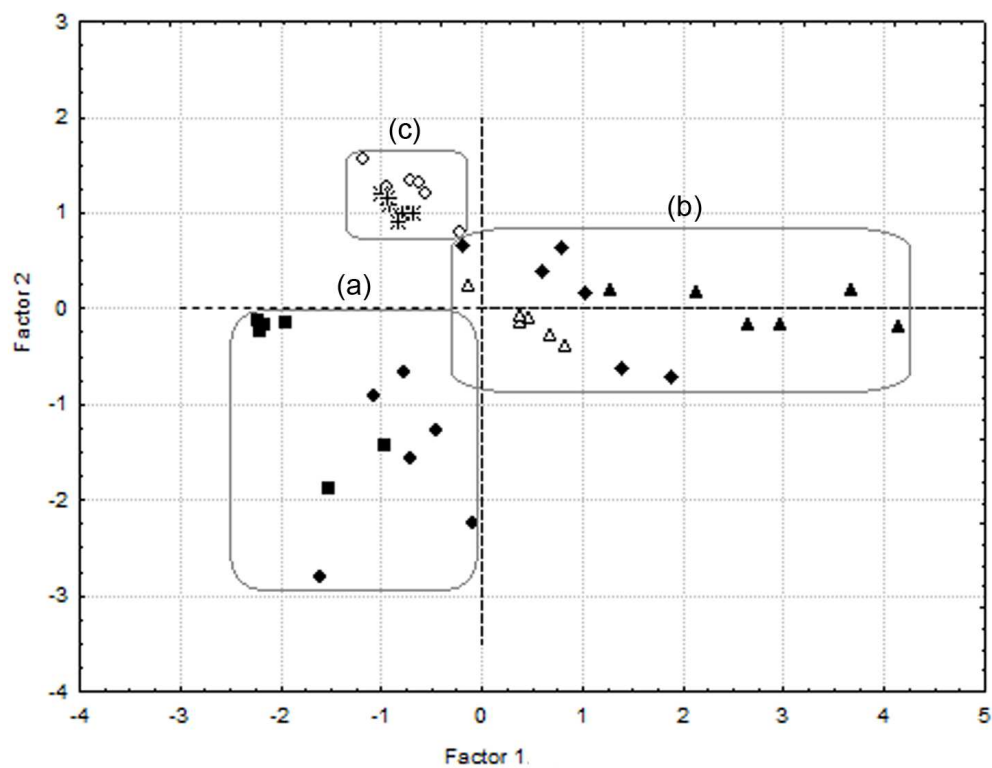


Figure 7  
123x95mm (300 x 300 DPI)



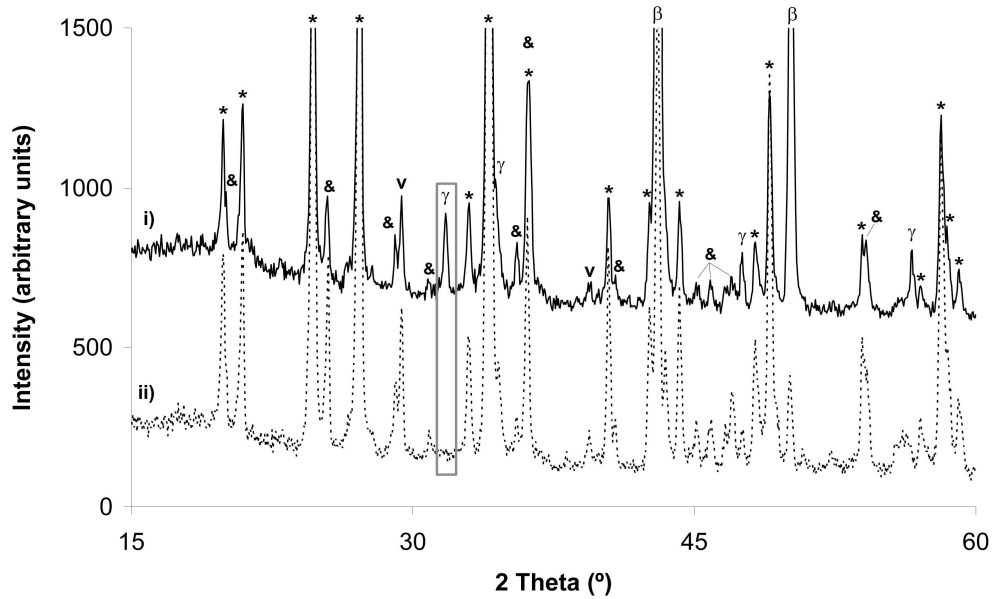


Figure 8  
253x156mm (300 x 300 DPI)

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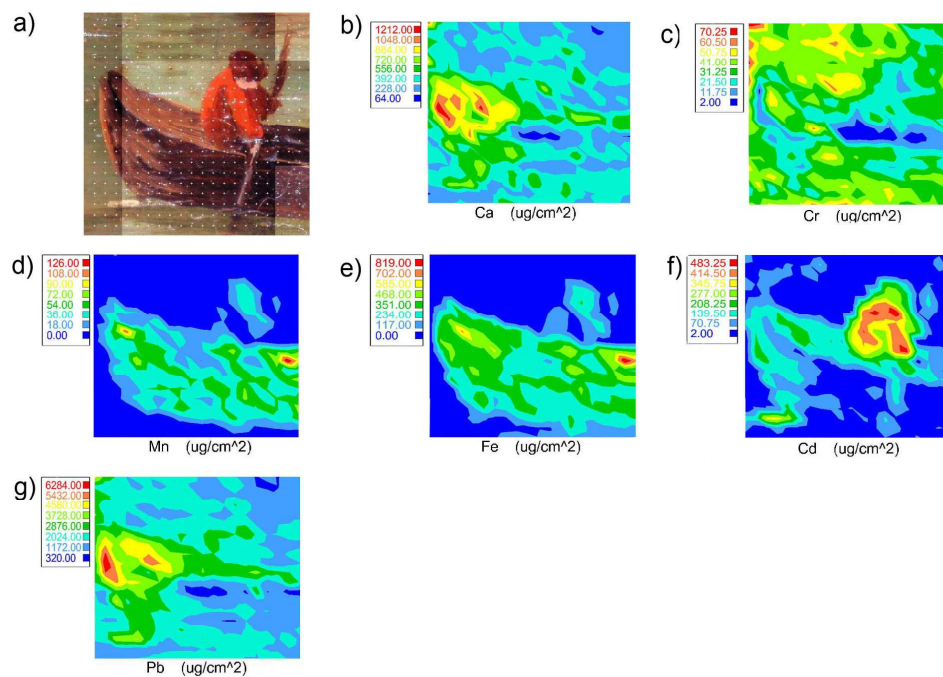


Figure 9  
170x116mm (600 x 600 DPI)

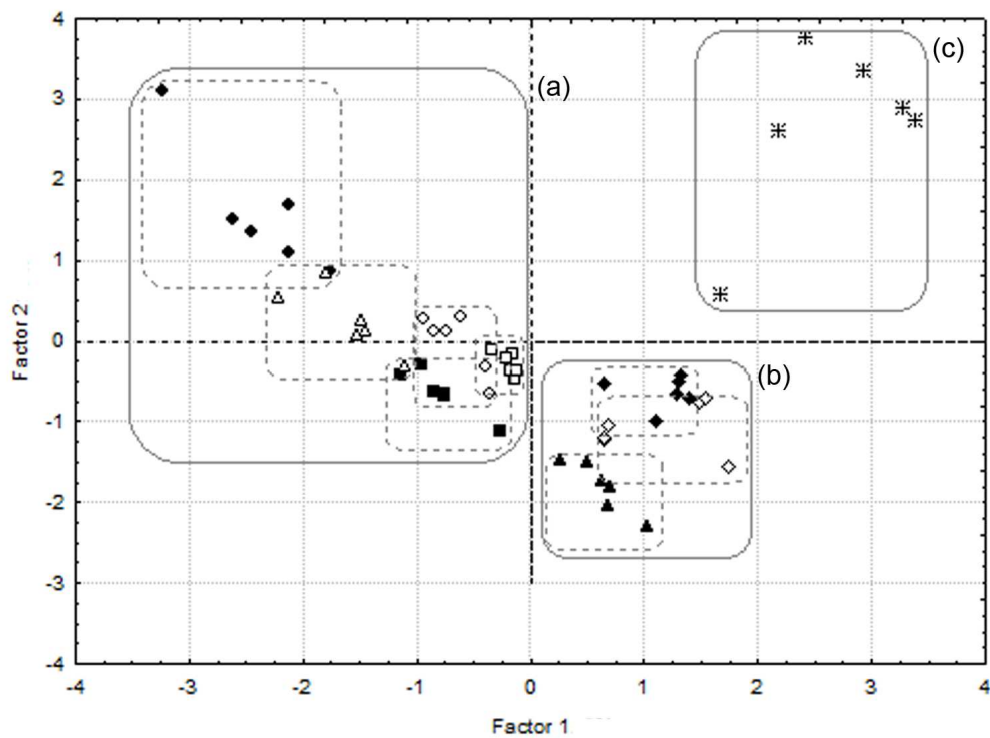


Figure 10  
127x95mm (300 x 300 DPI)

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