



First results on the use of a EDXRF scanner for 3D imaging of paintings

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ABSTRACT

A 3D map of chemical elements distribution from energy-dispersive X-ray fluorescence (EDXRF) analysis would be a perfect conclusion in a detailed study of any type of artifact. This map can be easily achieved by using synchrotron light as source of radiation, and micro-optics both at the source and at the detector. In such a manner a micro-voxel is irradiated and detected, which can be at any depth with respect to the surface of the artifact. This method is effective but needs a high-intensity X-ray source; therefore, its use in archaeometry is limited. An alternative method is proposed in the present paper, which uses a portable EDXRF-device to measure the altered K_{α}/K_{β} or L_{α}/L_{β} -ratios, which allow to locate the chemical elements. Several examples are described.

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Keywords: EDXRF, Scanner, X ray peaks ratio, paintings

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1. INTRODUCTION

Many artefacts have a multilayered structure: not only all types of paintings, which are composed by at least two-three layers, but also gilded or silvered metals, tumbagas (poor gold-alloy subject to depletion gilding), bronzes with patina, corroded silver and so on. The most useful analytical information about these multilayered structures can only be three-dimensional, although the third dimension is of the order of mm for paintings and of a few micrometers for metals.

2D scanning of paintings using energy-dispersive X-ray fluorescence (EDXRF) analysis, are currently carried out, by using collimated X-ray beams (μ EDXRF). In such a manner, maps of chemical elements in a painting are obtained, strongly increasing the level of information. 2D scanning are carried out in the best manner by using synchrotron radiation, but also X-ray tubes may be employed, due to the general high concentration of chemical elements in pigments [1, 2, 3,4].

EDXRF-analysis is also able to reconstruct a 3D-map of the elemental distribution by a confocal set-up realized by adding two optics in the excitation (synchrotron light) and in the

detection channel [5, 6, 7, 8]. However, this approach requires a high intensity X-ray source and the related device is, of course, not portable. Therefore, an alternative approach has been developed, based on the use of a portable EDXRF-equipment [9] and accurate analysis of the ratios of X-rays emitted by the chemical elements, which depends on the position and, in many cases, can help to reconstruct a 3D-image of the artefact. Figure 1 shows how EDXRF-analysis versus depth works in confocal configuration and using the X-ray ratios.

The EDXRF-spectrum of an irradiated and analyzed volume of a painting contains the X-ray peaks of all elements present in that volume, with a dependence on the depth from which X-rays of the element are coming. In several cases, and when the number of pigment layers is not too great, this dependence of X-ray peaks from the depth can be determined, by carefully processing the X-ray spectrum, in terms of elemental K_{α}/K_{β} and/or L_{α}/L_{β} -ratios [10]. In fact, these ratios depend on the location in the corresponding elemental layer, according to all the attenuation processes to which the X-rays emitted by this

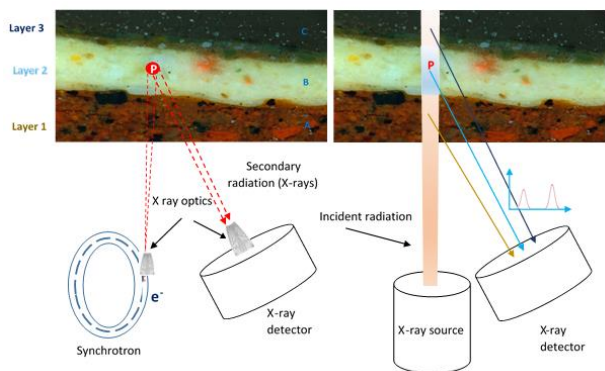


Figure 1. Left image: micro-EDXRF-analysis in confocal configuration: a micro-volume is identified by two optics at the X-ray source and detector, and a 3D-map is obtained when moving the measuring table orthogonally with respect to the artefact to be scanned. Voxels at any depth are then analyzed. Right image: all chemical elements excited in the truncated cone can reach the detector and no information is obtained about the originating depth, unless the internal X-ratios are processed; in fact, X-rays emitted by an internal point (P) are characterized by their altered K_{α}/K_{β} or L_{α}/L_{β} -ratios, which allows to correctly localize it and, finally, to obtain a 3D-image.

element are subject, i.e. self-attenuation in its own layer, and attenuation by the other superimposed layers. The real novelty of this work is in the proposal of a procedure for reconstruction of 3D images from XRF spectra processing, with the extraction of characteristic peaks for each element and the calculation of the thickness of each layer by systematically using the peak ratios. The image is not reconstructed automatically but iteratively on the base of structural model of artefact that could be modified taking into account the obtained results.

In this paper, some examples are given of 3D reconstruction of paintings and of alloys subject to some surface alteration or discontinuity.

2. THEORETICAL BACKGROUND

2.1. K_{α}/K_{β} and L_{α}/L_{β} -ratios

K_{α} are defined as the X-rays produced by transitions from the $n = 2$ to $n = 1$ atomic levels. K_{β} are the X-rays produced by transitions from the $n = 3$ to $n = 1$ atomic levels [10, 11]. L_{α} may be defined as the X-rays produced by transitions from the $n = 3$ to $n = 2$ level, and L_{β} are the X-rays produced by transitions from the $n = 4$ to the $n = 2$ level [10, 11].

The K_{α}/K_{β} and L_{α}/L_{β} -ratios for all elements have been calculated and in several cases were measured [13]. Theoretical values are calculated for infinitely thin samples, i.e. when secondary interactions in the sample are negligible. This corresponds to very low thicknesses, generally lower than 1 μm . The ratios K_{α}/K_{β} and L_{α}/L_{β} can vary:

- when the considered elemental layer is not “infinitely thin” (self-attenuation effect); this effect depends on the self-attenuating material and thickness [11, 13];
- when a layer of different material is covering the considered element; this effect depends also on the attenuating material and thickness [10].

In a multi-layered sample, K_{α}/K_{β} and L_{α}/L_{β} ratios allow, therefore, to measure the position of any element and the position and thickness of the corresponding layer. The thickness can be also determined from the attenuation of individual K_{α} or K_{β} (or L_{α} and L_{β}). This is strictly true for metal layers [10]. For pigment layers, where the pigment contains one or more chemical elements, an “equivalent thickness” may be determined,

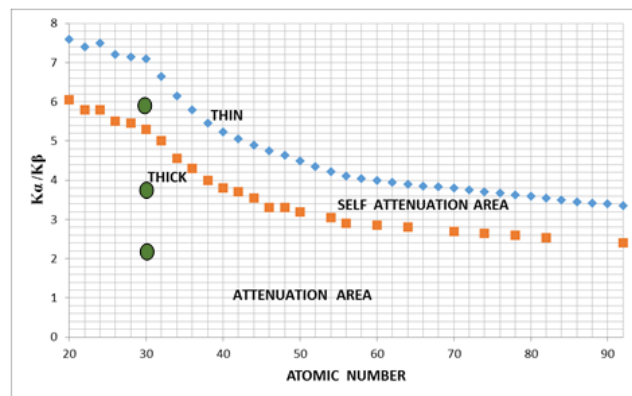


Figure 2. K_{α}/K_{β} peaks ratios vs atomic number for thin and thick samples [9]. Green point are results of measurements of Zn K peaks ratios (see Figure 7).

i.e. the elemental (metal) thickness which would give the same attenuation as the pigment [10].

In Figure 2 the average K_{α}/K_{β} ratio versus atomic number Z , for infinitely thin (blue rhombi) and thick (red squares) single element layer. The points for thin layers were deduced from various calculations. The points for thick layers were calculated according to the following equation: $(K_{\alpha}/K_{\beta})_{\text{thick}} = (K_{\alpha}/K_{\beta})_{\text{thin}} \cdot \mu_2 / \mu_1$, where μ_1 and μ_2 are the attenuation coefficients at energy of K_{α} and K_{β} radiation respectively. The possibility to measure an elemental thickness by self-attenuation is related to the difference between thin and thick samples. The area between thin and thick curves defines the self-attenuation region, while the region below the thick sample defines the attenuation by a second layer, when the first one is thick. When the first layer is not thick, then the attenuation region starts at the corresponding value.

The green points in the figure show the K_{α}/K_{β} ratio of Zn (white zinc pigment “wzp” of intermediate thickness), of wzp covered by a red pigment “rp” containing Se and Cd (wzp+rp), and finally of wzp + rp covered by a green pigment containing Cu and Br.

Figure 3 shows the average L_{α}/L_{β} ratio versus atomic number Z , for infinitely thin (blue) and thick (red) single element layers. The points for thin layers were deduced from various calculations. The points for thick layers were calculated according to the following equation: $(L_{\alpha}/L_{\beta})_{\text{thick}} = (L_{\alpha}/L_{\beta})_{\text{thin}} \cdot \mu_2 / \mu_1$, where μ_1 and μ_2 are the attenuation coefficients at energy of L_{α} and L_{β} radiation respectively. The possibility to measure an elemental layer thickness from self-attenuation is connected to the different response between thin and thick samples. The area between thin

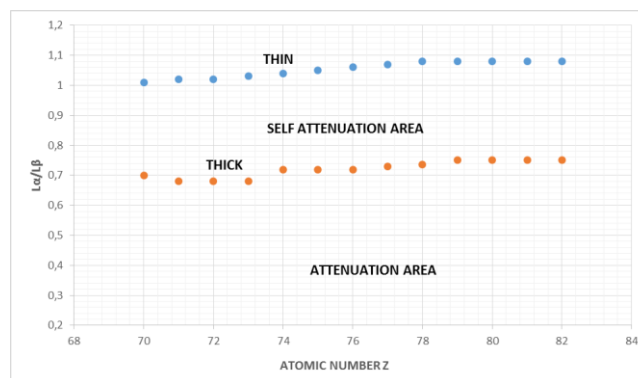


Figure 3. L_{α}/L_{β} ratios vs atomic number for thin and thick samples [10].

and thick curves defines the self-attenuation region, while the region below the thick sample defines the attenuation by a second layer, when the first one is thick. When the first layer is not thick, then the attenuation region starts at the corresponding value.

3. EXPERIMENTAL SET-UP

The experimental set-up for scanning a painting to obtain a 3D-Image is mainly composed of (Figure 4):

- a well collimated X-ray beam, mono energetic or bremsstrahlung, generated by a synchrotron or by an X-ray tube [9]; this incident beam irradiates the painting surface orthogonally;
- a well collimated X-ray detector, with excellent energy resolution and efficiency [14]; the detector collects X-rays at an angle ϑ as close as possible to the normal of the painting surface;
- the angle ϑ between surface normal and detector;
- a x-y movable table to translate the painting in the x-z plane;
- a sophisticated software to process with high accuracy and precision the X-rays spectra [15]; more into details, a complex set of X-rays is generally collected in the detector and processed in the pulse height analyzer. This complex spectrum requires to be processed by the software, in order to determine the chemical elements present in the picture and to quantitatively evaluate the K_{α}/K_{β} and/or L_{α}/L_{β} - ratios of these elements (Figure 5).

A test sample was realized using the following pigments spread on a wood substrate (Figure 6):

- a first layer of white Zinc of average thickness d_1 ;
- part of the first layer covered with a protective plastic layer, of mean thickness d_2 ;
- a second layer of a green pigment composed of copper and bromine, of mean thickness d_3 ;
- a third layer of red pigment containing selenium and cadmium, of mean thickness d_4 .

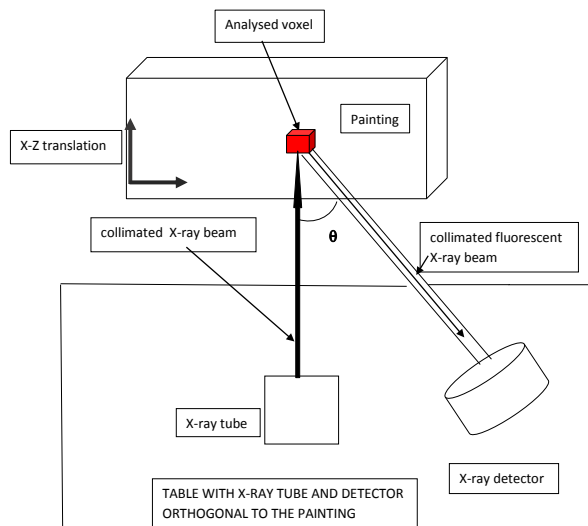


Figure 4. Experimental set-up to scan a painting composed of various pigment layers. It is composed of a collimated X-ray beam emitted by an X-ray tube and a collimated Si-drift detector that collect the secondary fluorescent X-rays. The intersection of the two beams identifies the irradiated and analyzed voxel of the painting. By moving the painting in the xz plane, the whole painting is EDXRF-analyzed.

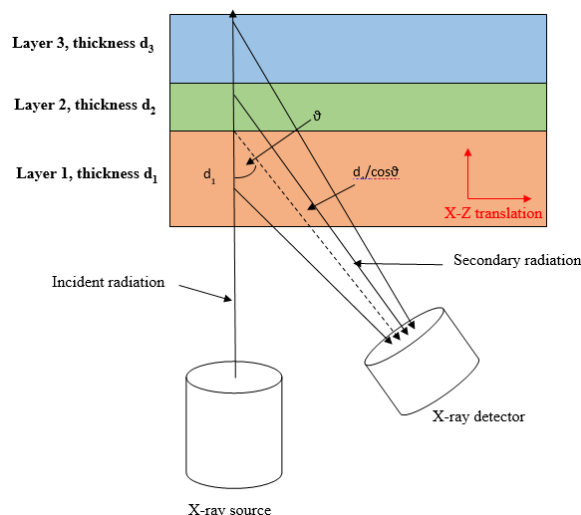


Figure 5. Layered structure of a painting composed of various pigments, and detection procedure.

The thickness inhomogeneity of the pigments was considered; for example, a layer of white zinc (area 4 in Figure 7) was measured in twenty different areas, giving the following result: $Zn(K_{\alpha}/K_{\beta}) = 6.0 \pm 0.2$, value internal to the self-attenuation area of Figure 2.

A linear scan of the painting surface is shown in Figure 7, where the values of $Zn(K_{\alpha}/K_{\beta})$ versus position are shown and where scanning was carried out in areas 1 to 4. Changes between points of the same pigment reflects the variable thickness of the pigments layer. The following average values were measured:

- $Zn(K_{\alpha}/K_{\beta}) = 6.0 \pm 0.1$ (zinc-white, area 4 in Figure 7),
- $Zn(K_{\alpha}/K_{\beta}) = 5.65 \pm 0.2$ (zinc-white covered by a protective resina, area 1 in Figure 4),
- $Zn(K_{\alpha}/K_{\beta}) = 4.6 \pm 0.25$ (Zn crossing the Br-pigment, area 3 in Figure 5),
- $Zn(K_{\alpha}/K_{\beta}) = 2.9 \pm 0.3$ (Zn crossing the Cd-Se pigment plus the Br-pigment, area 2 in Figure 7).

Then, from the relative intensity of zinc-lines, attenuated and not, the approximate thickness of Br and Cd-pigments can be calculate; it ranges between $80 \mu m$ and $110 \mu m$ for the Cd-Se pigment and between $60 \mu m$ and $100 \mu m$ for the Br-pigment.

Similar results were obtained using a test sample involving L transitions, having the following sequence of pigment layers (starting from the wood substrate): white lead, bromine pigment, cadmium – selenium pigment. Scanning of this sequence gave the results for the $Pb(L_{\alpha}/L_{\beta})$ ratio shown in Figure 8. Differences of $Pb(L_{\alpha}/L_{\beta})$ ratio inside the same pigment reflects the thickness variation of the pigment layer.

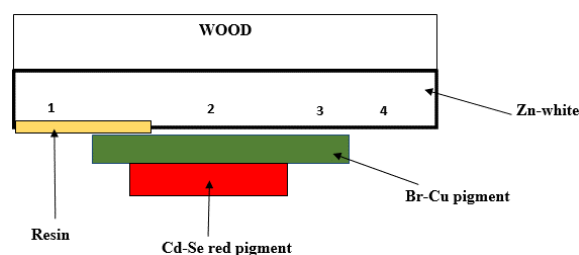


Figure 6. Pigment layers; from the surface: zinc-white, Br-Cu pigment, Cd-Se red pigment. On the left side, Zn-white is covered by a protective resin.

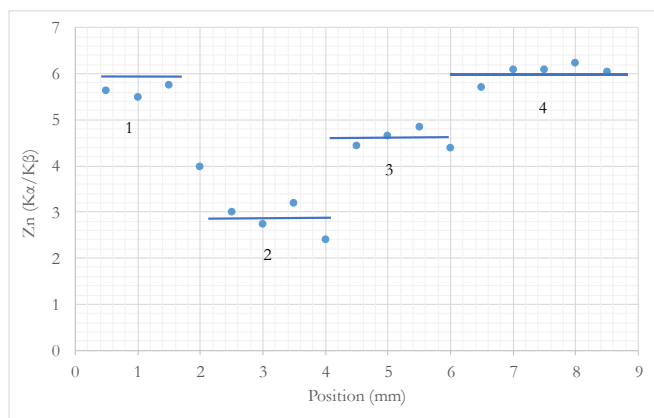


Figure 7. Linear scanning of Zinc (K_{α}/K_{β}) ratio, for the set of pigments shown in Figure 5.

The following average values were measured:

- $Pb(L_{\alpha}/L_{\beta}) = 0.8 \pm 0.02$ (lead-white),
- $Pb(L_{\alpha}/L_{\beta}) = 0.45 \pm 0.03$ (Pb crossing the Br-pigment),
- $Pb(L_{\alpha}/L_{\beta}) = 0.36 \pm 0.03$ (Pb crossing the Cd-Se pigment plus the Br-pigment).

In many cases a 3D-map is not required, and the described methods for the evaluation of the self-attenuation and attenuation effects, were largely employed in the case of gilding, silvering, tumbaga and so, by using single measurements only [10, 16, 17, 18]. The same method was applied in the case of the halos of Giotto's fresco in the chapel of the Scrovegni in Padua, where the multilayered structure was reconstructed, on the basis of K - and L -internal ratios [19].

In conclusion, accurate evaluation of K - and L -internal ratios when carrying out EDXRF scanning of a multilayered artifact is able to generate 3D imaging.

4. PROPOSED PROCEDURE TO OBTAIN A 3D IMAGE

The following step-procedure is proposed to obtain a 3D-imaging of a painting:

- 1) Scanning of the painting or of an area of a painting with an adequate space resolution
- 2) Processing the EDXRF-spectra with a proper software
 - 2.1) Determining the elements of interest present in the spectra
 - 2.2) Determining the area of the K - (K_{α} and K_{β}) or L - (L_{α} and L_{β}) peaks of these elements
 - 2.3) Analysing the K_{α}/K_{β} and L_{α}/L_{β} -ratios with a dedicated software
- 3) According to point 2.3, classification of the elements versus depth
- 4) According to point 2.2, calculation of the layer thickness
- 5) According to point 2.2, a 3D-map of chemical elements can be constructed.

5. CONCLUSIONS

The simplicity with which a scanning system can currently be realized and the information that can be obtained by using it in the case of a stratified object (such as a painting), implies that its use will quickly become a rule rather than an exception.

In this context it is important, as previously done for many microanalytical techniques, to verify which additional information can be extracted from the acquired data, in addition to elemental maps of various elements at the surface.

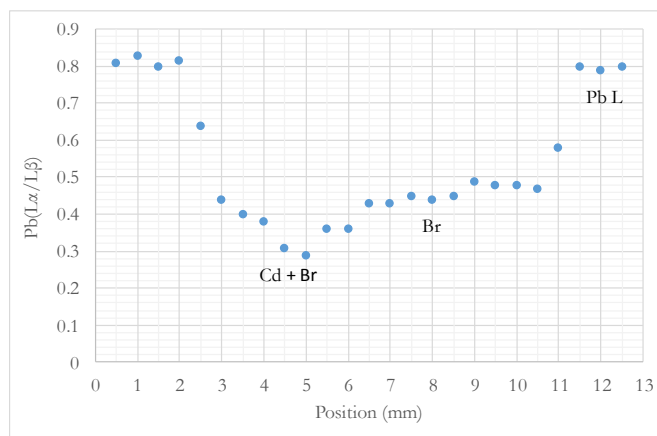


Figure 8. Linear scanning of $Pb(L_{\alpha}/L_{\beta})$ ratio. From left: $Pb(L_{\alpha}/L_{\beta}) \sim 0.8$, for Pb alone; Pb covered by a pigment containing Cd, plus a pigment containing Br, $Pb(L_{\alpha}/L_{\beta}) = 0.36$; Pb covered by a pigment containing Br, $Pb(L_{\alpha}/L_{\beta}) = 0.45$; Pb alone, $Pb(L_{\alpha}/L_{\beta}) = 0.8$.

This work shows how it is possible to obtain, in addition to the traditional elemental maps, also maps of the ratios between peaks of the same spectrum that contain various additional information.

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