Research Article

X-Ray Spectrometry

Received: 14 July 2010 Revised: 6 September 2011 Accepted: 21 September 2011 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/xrs.1373

In situ energy dispersive X-ray fluorescence analysis of rock art pigments from the 'Abrigo dos Gaivões' and 'Igreja dos Mouros' caves (Portugal)

M. J. Nuevo,[a]* A. Martín Sánchez,[a] C. Oliveira[b] and J. de Oliveira[b]

A portable energy dispersive X-ray fluorescence spectrometer was used to obtain the elemental composition of Neolithic rock art paintings of the 'Abrigo dos Gaivões' and 'Igreja dos Mouros' caves. These caves, located in the Esperança parish, Arronches' county, in the San Mamede's mountains (Portugal), belong to a group of spread shelters just next to the western Spanish border. Results show the strong presence of iron in bare rock, and this element can be clearly detected as the main component of the red paintings. No evidence of manganese was detected in either the brownish or the black paintings, contrary to other Neolithic paintings in the Mediterranean area. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: EDXRF; portable systems; non-destructive analysis; *in situ* measurements; rock art paintings

Introduction

The application of scientific techniques and methods to the study of historical and cultural heritage has remarkably advanced our knowledge of human civilization. Non-destructive techniques for analysis of components of a sample are very useful and fully necessary when the samples are unique, such as the works of art and archaeological structures belonging to the historical and cultural heritage. In the last decades, huge efforts have been made on improving equipment that can be used to carry out non-destructive and non-aggressive experiments in open air.[1] Energy dispersive X-ray fluorescence (EDXRF) techniques have become one of the very useful non-aggressive methods being widely used. Furthermore, the impossibility of carrying works of art to the laboratory (e.g. fresco painting) has recently promoted the development of portable devices in order to perform measurements *in situ*.[2–5]

A portable EDXRF has been designed and constructed in our laboratory, and it has been used to study the elemental composition of Neolithic rock art paintings of the 'Abrigo dos Gaivões' and 'Igreja dos Mouros' caves (Portugal). These caves, located in the Esperança parish, Arronches' county, in the San Mamede's mountains, belong to a group of spread sites just next to the western Spanish border.

In the Iberian Peninsula, a similar kind of rock art manifestation has also been found in different areas, especially in the north part, called the Cantabrian region, where the outstanding world-famous Altamira caves are found, and also in the Mediterranean (Levantine) zone. In the latter area, similar EDXRF studies have been carried out on red and black paintings.[6,7]

In the Portuguese paintings, although animal and human figures are the essential elements represented in the two studied shelters, other configurations, such as several symbols, are also depicted.[8–10] Although the predominant colour in these paintings is red, different red tones and some black signs can be observed. Moreover, a peculiar white painting from the 'Igreja dos Mouros' cave has also been analysed. In this work, the results of the EDXRF analyses, their discussion and the conclusions reached with these studies are presented.

Materials and Methods

The 'Abrigo dos Gaivões' and 'Igreja dos Mouros' caves, situated in one of the extremes of the São Mamede's mountains (Esperança, Arronches, Portugal), belong to a group of spread caves just next to the western Spanish border. The 'Abrigo dos Gaivões' is located at 657 896.25 E–4 334 892.75 N UTM coordinates and 365 m over the sea level with a south orientation. In this cave, two series of figures can be distinguished: the occidental and the central panel (see Figs 1 and 2, respectively). Although red is the predominant colour in both panels, different tones of this pigment can be clearly observed. Moreover, other figures in black colours, mainly in the central panel, can be also observed. On the other hand, in the 'Igreja dos Mouros' cave, situated at 657 459.46 E–4 335 104.99 N UTM coordinates and 423 m over the sea level with a southeast orientation, a set of red figures are painted on the cave walls. However, in this cave the attention should be focused on a white small painting, which is very unusual in this area (Fig. 3).

* Correspondence to: M. J. Nuevo, Departamento de Física, Universidad de Extremadura, Avenida de Elvas s/n, 06071 Badajoz, Spain. E-mail: maria@unex.es

a Departamento de Física, Universidad de Extremadura, Avenida de Elvas s/n, 06071 Badajoz, Spain

b CHAIA–Universidade de Évora, 7000 Évora, Portugal

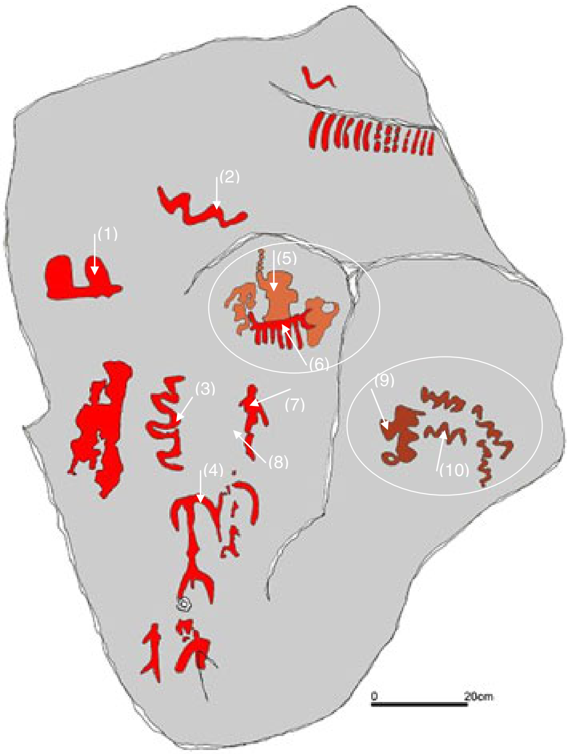

Figure 1. Schematic representation of the occidental panel from the 'Abrigo dos Gaivões' shelter, with the studied points indicated.

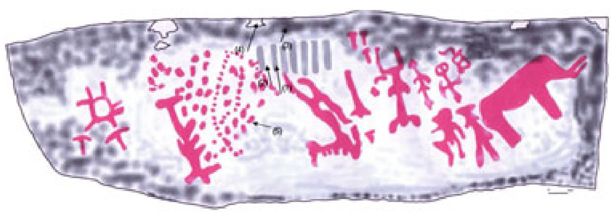

Figure 2. Schematic representation of the central panel from the 'Abrigo dos Gaivões' shelter, with the studied points indicated.

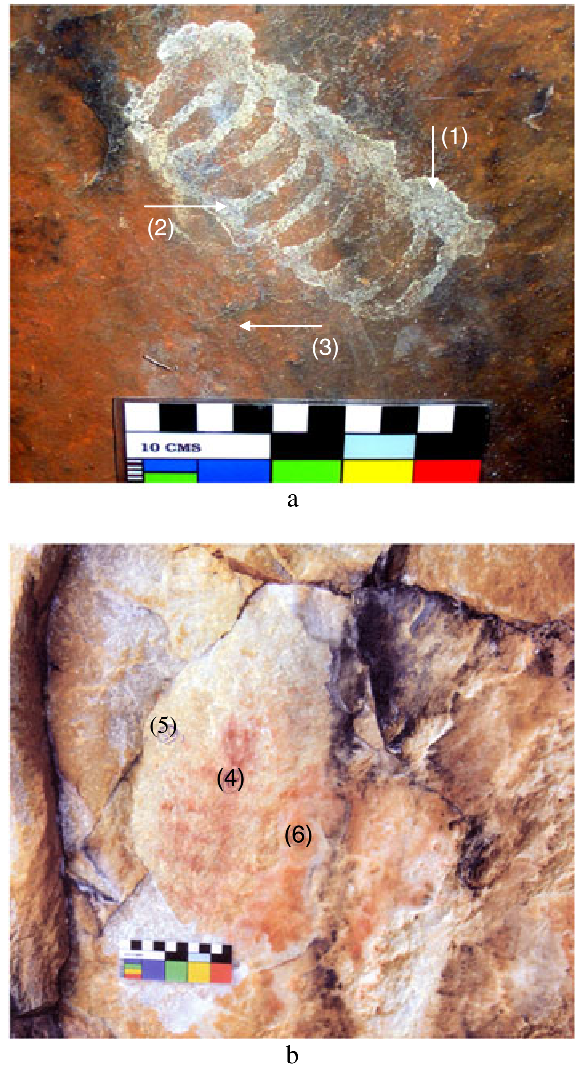

Figure 3. Figures from the 'Abrigo dos Mouros' cave: (a) white figure and (b) red figure, with the analysed points indicated.

In order to acquire the *in situ* spectra, an EDXRF spectrometer developed at the University of Extremadura was directly used on the points of interest. This portable spectrometer was composed of a self-contained miniature X-ray tube (ECLIPSE III, Amptek, Inc., Bedford, MA), a thermoelectrically cooled detector (XR-100CR, Amptek Inc.) and a crossed lasers system. The bias source connected to the tube was operating in a continuous range up to 30 kV and 100 μA and generating an X-ray beam from a solid grounded Ag anode, which was collimated in order to produce on the sampled site a spot of 1.5 mm in diameter, according to the manufacturer's specifications. These characteristics were obtained with a tube of low dimensions (16.8 cm × 3.8 cm) and light weight (300 g), which are remarkable features as far as portability is concerned.[11] Despite the size and the weight being too small, the energy of the produced X-ray was large enough to excite the characteristic K and L X-ray lines of the elements present in samples with atomic number greater than that of sodium. The elements of interest were identified by their characteristic energies of emission lines in the range from 0 to 25 keV.

The fluorescent X-rays were collected in a solid-state Si-PIN Peltier-cooled detector with a 1-mm Be window, with an active area of 25 mm^2 and a thickness of 300 μm. The nominal energy resolution of this detector for ^{55}Fe peak was 220 eV (FWHM) at 5.9 keV. The detector, preamplifier and cooler were jointly included in the same device connected to an amplifier provided with the bias supply. Signals were recorded with an Amptek multichannel analyser into a portable PC. The whole system was powered by a 950-W portable fuelled gasoline generator.

In order to locate the points of interest on the sample surface, a system composed of a level laser crossed with a pointer laser was arranged to determine the intersection point of the incident X-ray beam and detector axis. All the components (tube, detector and lasers) were fixed on a flat surface (22 cm × 32 cm), with the proper geometry obtained after several tests on distances, incident angles on the sample and angles between primary and secondary X-rays. From previous studies, a well-balanced compromise among all the degrees of freedom was reached. Optimal geometry was chosen with the primary beam normally incident to the sample at a distance of 1.5 cm, with the detector pointing at an angle of 45° between the sample surface and the detector.

The fluorescence peak analysis of the obtained spectrum in each point allows identifying the chemical elements present on the sampled surface. This was achieved using the WinQxas [12] code. In order to diminish the influence of fluctuations in the tube intensity and uncertainties in the geometrical disposition of the sampled surfaces, the net area of each registered peak was normalized to the total area of its corresponding whole spectrum.

Results and Discussion

Figures from the 'Abrigo dos Gaivões' cave

Occidental panel

The occidental panel is composed of several figures with clear differences in shape and colour, with some of them forming groups, as shown in the schematic representation in Fig. 1. Although the red colour is predominant in the panel, a group of three orange figures and a brownish group of five elements can also be distinguished. With respect to the shape, not only anthropomorphic schematizations and zoomorphic and serpentiform representations but also some elements of non-identified shape can be observed. For instance, in the upper part, where no spectral analyses were carried out because of the impossibility of the access, a set of 13 sticks is presented, which could suggest some kind of calendar. Supportive to this hypothesis is the fact that in the upper part outside the cave (not shown in the figures), another set of 24 sticks grouped in four files of seven signals each (moon month?) was also clearly distinguished, painted with red colour in the walls. In contrast, some animal shapes seem to be depicted in the sampled points denoted by 1, 2, 3, 6, 9 and 10.

Table 1 presents the peak net areas normalized to the total area for the different analysed points. The spectra are composed of 10 points in the figures (F01–F10) and 5 points in the rock (R01–R03, R09–R10), where the number means the proximity to the corresponding point figure. A total of 10 elements (P, S, K, Ca, Ti, Cr, Mn, Fe, Cu and Zn) were identified, although S was detected only in the spectrum corresponding to point F09, and Cr only in F07, F10 and R09. On the other hand, in all the analysed spectra, not only in the painting but also in the rock close to it, the highest peak corresponded to Fe, which suggests that iron is a major component of the rock. Although iron is present at high amounts in the rock, it is possible to consider that the red pigments in the paintings also contained high amounts of iron, as can be observed by the average value in the figures, $\langle Fe_{fig} \rangle = 0.221 \pm 0.080$, compared with that obtained for rock points, $\langle Fe_{rock} \rangle = 0.138 \pm 0.060$. This fact confirms the initial supposition that the red colour of the rock painting is mainly due to the hematite, a mineral composed of iron oxide, which can be traced with other elements such as Ti, Mg and Cu, among others.

Titanium is the other element present in all the spectra. No significant differences can be observed in the values quoted in Table 1, whose averages in the figures, $\langle Ti_{fig} \rangle = 0.004 \pm 0.002$, and rock points, $\langle Ti_{rock} \rangle = 0.004 \pm 0.001$, suggest that titanium is not a pigment component but a nude rock component. In a similar way, the presence of calcium should be understood in the analysed spectra because although a wide range of values is obtained, no correlation between the rock and figure points has been observed, suggesting that the presence of calcium must be due to the rock instead of the paintings.

The presence of phosphorus is detected in 7 of the 10 figure points, compared with only 2 of 5 rock points. A possible hypothesis is that phosphorus in shelters could be present due to bird excrements, although our results seem to indicate that phosphorous is a component of the pigments of the painted figures. However, this statement needs additional studies.

On the other hand, the iron content in F05 is lower than that in the other figures. Moreover, phosphorus and cuprum are also clearly observed in this point. Both evidences seem to be related with the orange (more than red) colour in the figure corresponding to F05, suggesting that this anthropomorphic scheme was painted in a different way or perhaps in a different time, compared with the rest of the panel. This is supported by the fact that the zoomorphic red figure (F06), depicting a dog,[9,10] seems to be over this human schematization of F05.

The colour in F09 and F10 seems to be darker than in the rest of figures. In general, the comparison of values from different elements does not give an explanation for this colour discrepancy,

Table 1. Comparison of the peak net areas, normalized to the total area for the analysed points, in the occidental panel

Point	P	S	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn
F01	0.0012	n.d.	n.d.	0.0134	0.0070	n.d.	0.0029	0.188	n.d.	n.d.
F02	n.d.	n.d.	n.d.	0.0110	0.0027	n.d.	n.d.	0.197	n.d.	0.0126
F03	0.0005	n.d.	n.d.	0.0130	0.0032	n.d.	0.0019	0.205	n.d.	n.d.
F04	n.d.	n.d.	0.0020	0.0086	0.0042	n.d.	n.d.	0.222	0.0066	n.d.
F05	0.0046	n.d.	n.d.	0.0011	0.0013	n.d.	n.d.	0.110	0.0120	n.d.
F06	0.0010	n.d.	0.0032	0.0015	0.0035	n.d.	n.d.	0.187	0.0022	n.d.
F07	n.d.	n.d.	0.0038	0.0007	0.0072	0.0015	n.d.	0.437	n.d.	n.d.
F08	0.0028	n.d.	0.0018	n.d.	0.0046	n.d.	n.d.	0.260	n.d.	n.d.
F09	0.0014	0.0006	0.0031	0.0085	0.0053	n.d.	0.0018	0.197	n.d.	n.d.
F10	0.0008	n.d.	0.0030	0.0050	0.0030	0.0011	0.0021	0.203	n.d.	n.d.
R01	n.d.	n.d.	n.d.	0.0130	0.0025	n.d.	0.0036	0.208	n.d.	n.d.
R02	n.d.	n.d.	n.d.	0.0079	0.0034	n.d.	0.0013	0.160	0.0053	0.0043
R03	0.0010	n.d.	n.d.	0.0092	0.0042	n.d.	0.0010	0.177	n.d.	n.d.
R05	0.0014	n.d.	n.d.	0.0017	0.0053	n.d.	n.d.	0.071	n.d.	n.d.
R09	n.d.	n.d.	n.d.	0.0025	0.0031	0.0036	0.0022	0.073	n.d.	n.d.

The spectra are composed of 10 points in the figures (F01–F10) and the corresponding points in the rock next to them (R01–R10). Uncertainties are in the order of the last significant figure (3rd decimal for Fe and 4th decimal for the rest of quantities).
n.d., no detected elements.

especially when iron and manganese contents are revised. A high manganese content was expected in these figures because the usual source of black Neolithic pigments is manganese oxide, as it has been found in black Levantine paintings.[6,7] In our case, the absence of a higher fluorescence peak of manganese in the figures suggests the use of charcoal or smoke black, which were also natural sources used for black pigments. This result can be seen as an advantage because these paintings should be suitable for ^{14}C dating.

Central panel

In contrast to the occidental panel where different red tones can be found, the central panel is configured only by red and black colours, as shown in the schematic representation in Fig. 2. Different anthropomorphic figures, digital symbols and a controversial zoomorphism, probably representing a wild boar, can be observed. In this case, because red figures seemed similar to those previously analysed in the occidental panel, our attention was focused on the black parts of the panel, with the analysed points indicated in the figure. In spite of the proximity of panels, the number of elements found in the occidental panel contrasts with only five elements (K, Ca, Ti, Cr and Fe) identified in the spectra of the central panel. Table 2 shows the net peak areas normalized to the total area of each spectrum.

Similar to the occidental panel, the highest fluorescence K_α peak corresponds to iron, with titanium being the other element present in all the analysed spectra. This fact should be a confirmation that the main components detected on the rocks in the cave are these two elements, as already supposed. Moreover, except in P4, potassium was also identified in all the spectra, in contrast to the occidental panel where it was only found in some painting spectra. In the central panel, the presence of potassium is clearly associated with the bare rock instead of the paintings. In the occidental panel, potassium was found only in 6 of 10 analysed painting points, and was a trace element compared with iron. This could indicate that the presence of K is due to the paintings, but no clear evidence has been obtained. Perhaps, the same hypothesis could be made about the presence of P and K in the paintings. However, more tests are needed to confirm this hypothesis. Finally, the similarity in the analysed spectra, together with the absence of manganese, suggests that the black figures from the central panel were made of charcoal, again offering the possibility of dating them.

Table 2. Comparison of the peak net areas, normalized to the total area for the analysed points, in the central panel

	K	Ca	Ti	Cr	Fe
P1	0.0056	n.d.	0.0032	0.0009	0.198
P2	0.0045	n.d.	0.0028	n.d.	0.200
P3	0.0039	n.d.	0.0021	n.d.	0.135
P4	n.d.	0.0040	0.0036	0.0038	0.074
P5	0.0012	0.0012	0.0078	n.d.	0.157

A total number of 5 points were analysed, denoted by P1–P5, all of them outside of the red paintings. Uncertainties are in the order of the last significant figure (3rd decimal for Fe and 4th decimal for the rest of quantities).

n.d., no detected elements.

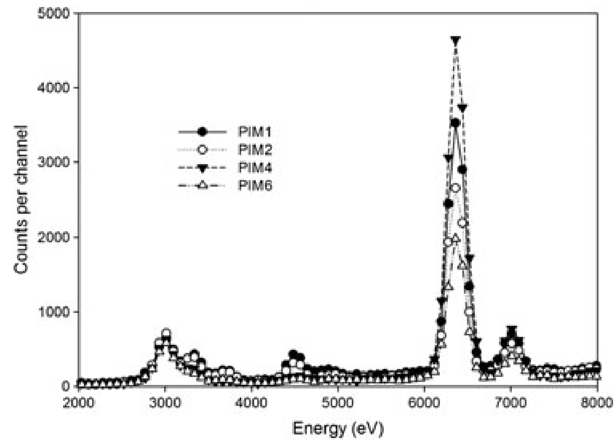

Figure 4. Spectral comparison of white painting (PIM1), its surrounding (PIM3), red painting (PIM4) and its surrounding (PIM6), all from the 'Abrigo dos Mouros' cave.

Figures from the 'Igreja dos Mouros' cave

This shelter is a shallow hole in the rock (2–3 m deep) with a very wide access, about 3 m high and 2 m wide, but narrowing at the end, with a small white painting as shown in Fig. 3a. Moreover, in the entrance to this cave, a red animal figure can also be distinguished (see Fig. 3b). In order to detect the elemental composition of these paintings, spectra on several points were acquired. In Fig. 3a, two of the spectra were taken on the figure (PIM1 and PIM2) and the third on the proximity of it, but on the rock (PIM3). In all these three spectra were identified six chemical elements (Si, K, Ca, Ti, Fe and Cu), and similarly to the former shelter, the highest fluorescence peak corresponded to iron, as can be seen in Fig. 4. In this figure, the spectrum from the red painting (PIM4, Fig. 3b) and that from the next bare rock (PIM6, Fig. 3b) are shown for comparison. The fluorescence iron peak in the bare rock in the proximity of the white painting (PIM3) is higher than that in the bare rock near the red picture (PIM6), as seen in Fig. 4, suggesting that the former is richer in iron compared with the latter. In this case, the iron ratio between the painting and the bare rock is maintained, indicating that the red colour is mainly due to iron oxide. However, when a comparison of the white picture (PIM1) with its surrounding (PIM3) is made, the behaviour is just the opposite, suggesting that the white painting is formed by a layer of organic components on the surface. Moreover, the natural source of white colour in Neolithic paintings seems to be calcium carbonate, which might cause calcium to be more abundant in the figures than in the bare rock. However, no evident differences in calcium peak between the figure and the bare rock were detected, although significant differences in the fluorescence K_α iron peak were found. Nevertheless, this white painting is a very peculiar and unusual figure not only in colour but also in shape, and thus demands further archaeological studies and the use of complementary analytical techniques to unmask its mysteries.

Conclusions

The use of a portable EDXRF spectrometer in the field to study the elemental composition of rock paintings is very important as a tool to identify paintings of different origins. In the case of the Neolithic paintings from 'Abrigo dos Gaivões' and 'Igreja dos Mouros', results indicate that iron coming from hematite is one of the major components of the painted figures, and was also found to be a component of the bare rocks. Titanium was also found in the bare rock. Manganese peaks were not found in the spectra coming from the black figures; therefore, the black pigment used to draw the figures or signs observed on the rock was probably made of charcoal or smoke black. To date, no explanation has been given regarding the white colour in one of the figures, although a gross shell of some organic compound was covering this figure.

Acknowledgement

Thanks are due to Drs. C. Roldán and J. L. Ferrero from the University of Valencia (Spain) for their help and useful comments.

References

[1] T. Calligaro, J. C. Dran, J. P. Poirot, G. Querre, J. Salomon, J. C. Zwaan, *Nucl. Instr. Meth. B* **2000**, *161*, 769.
[2] G. Pappalardo, J. de Sanoit, A. Musumarra, G. Calvi, C. Marchetta, *Nucl. Instr. Meth. B* **1998**, *109*, 214.
[3] G. Pappalardo, E. Costa, C. Marchetta, L. Pappalardo, F. P. Romano, A. Zucchiatti, P. Prati, P. A. Mandò, A. Migliori, L. Palombo, M. G. Vaccari, *J. Cult. Herit.* **2004**, *5*, 183.
[4] A. G. Karydas, H. Brecoulaki, T. Pantazis, E. Aloupi, V. Argyropoulos, D. Kotzamani, R. Bernard, C. Zarkadas, T. Paradellis, in X-ray for Archaeology. Springer, Netherlands, **2005**. ISBN: 978-1-4020-3580-7
[5] P. J. Potts, M. West (Eds) Portable X-Ray Fluorescence Spectrometry: Capabilities for *In situ* Analysis. RSC Publishing, Cambridge, **2008**. ISBN: 978-0-85404-552-5
[6] C. Roldán, S. Murcia-Mascarós, J. Ferrero, V. Villaverde, R. Martínez, P. Guillem, E. López, **2006**, Presented at the European Conference on X-Ray Spectrometry (*EXRS-2006)*, Paris.
[7] C. Roldán, S. Murcia-Mascarós, J. Ferrero, V. Villaverde, E. López, I. Domingo, R. Martínez, P. Guillem, *X-Ray Spectrom*. **2010**, *39*, 243.
[8] H. Breuil, La roche peinte de Valdejunco à la Esperança, prés de Arronches (Portalegre), Terra Portuguesa, Lisboa, **1917**, pp. 17.
[9] C. Oliveira, J. De Oliveira, Percurso Historiográfico do Complexo de Arte de Arronches, *Actas do III Taller Internacional de Arte Rupestre*, Havana, Fundación António Núnez Jiménez de la Naturaleza y el Hombre, ed. Electrónica, **2008**.
[10] C. Oliverira, As pinturas rupestres de Arronches, Master degree in Archaeology and Environment, Evora University, **2010**.
[11] C. Caneva, M. Ferretti, Proceeding of 15th World Conference on Nondestructive Testing, *(15th WCNDT)*, Roma, **2000**.
[12] Quantitative X-Ray Spectra Analysis System (WinQxas), Version 1.3. International Atomic Energy Agency. Vienna, **2001**.

