

## A portable X-ray fluorescence device for *in situ* analyses of mural paintings

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**Summary.** — Within the context of a research program for studying with non-destructive methods the preparation and realisation techniques of mural paintings used in the Roman age, a portable ED-XRF device for elemental analysis has been set up. Preliminary tests have been carried out on two Roman mural paintings belonging to the Baia Archaeological Complex (Naples). Datable to different periods, the two paintings show different manufacturing and conservation states, thus representing a good test for verifying the ED-XRF device capability. *In situ* and laboratory measurements, performed on materials of different origin and nature, have permitted the determination of the pigments and the recognition of pollution traces.

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PACS 81.70.-q – Methods of materials testing and analysis.

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### 1. – Introduction

The study of conservation state, composition and manufacturing methods of the works of art must precede any operation on them. An expert restorer can perform very good,

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but qualitative analyses. Only the technical analyses give precise, quantitative, punctual information. Several diagnostic tools have been realised for this purpose, among which *in situ* energy dispersive X-ray fluorescence is very powerful. First of all it is absolutely non-destructive. Then it allows to perform easily and in a short time the elemental analysis of the art work surface layer, which is influenced by corrosion, atmospheric pollution and other physical and chemical changes due to ageing. *In situ* energy dispersive X-ray fluorescence is strongly recommended as the first approach to the diagnostics of an art work. Often it is sufficient to get the inquired information, otherwise specific tiny samples can be taken from the work of art for further laboratory analyses (microdestructive analyses) [1-4].

In this paper we present a very compact and versatile energy dispersive X-ray fluorescence (ED-XRF) portable device realised with commercial equipment. Portable ED-XRF systems have already been constructed in several Laboratories, but the continuous technological improvements allow nowadays the realisation of small systems easy to be carried around and with a high performance, possibly dedicated to the study of specific problems [5-7].

The ED-XRF device described below has been tested in the study of the pigments and the pollution effects occurred on Roman wall paintings located in the Baia Archaeological Complex, near Pozzuoli (Naples). The tests have shown the very good performance of this instrument, which has recently been implemented with a polycapillary X-ray lens [8]. Obviously, this ED-XRF device can be used for studying any other work of art.

## 2. – Experimental

In energy dispersive X-ray fluorescence spectroscopy the sample is irradiated with an X-ray primary beam and the emitted fluorescence photons are collected and analysed. The elements contained in the sample are deduced from the energies of the fluorescence X-ray multiplets. The relative intensities of the lines can be compared between spectra measured on different samples, and the changes of the concentration of elements can be deduced in a semi-quantitative way. In many cases ED-XRF allows to identify the pigments used for mural paintings [9, 10].

The portable device, shown in fig. 1, is composed by an X-ray tube, an X-ray detector and an electronic chain. The characteristics of each component are reported in table I. The instrument is completed by a small electricity generator, necessary in the archaeological sites where electricity outlets are not available.

The primary X-ray beam, emitted by the X-ray generator, is collimated with a tantalum diaphragm, which can be changed with a bayonet system. Tantalum has been chosen since it is a high- $Z$  element; thus a very thin sheet (0.5 mm thick) is sufficient to stop the X-rays supplied by the X-ray generator and we never observed spurious Ta L emission lines in the spectra. The diaphragm is located at 50 mm from the X-ray generator focus and it is 25 mm far from the sample surface. In this work we used a diaphragm with a 1 mm diameter hole in order to obtain an X-ray spot of about  $1.5 \text{ mm}^2$  on the sample. This spot allows to point the desired area at the best, without being sensitive to the microscopic non-homogeneity of the sample.

A second collimating system is placed in front of the detector for improving the resolution and reducing the background signal. This collimator is made with two tantalum diaphragms, one attached to the detector window and the other at 20 mm from it. With 2 mm diameter holes, the opening angle of the collected fluorescence beam is about  $5^\circ$ .

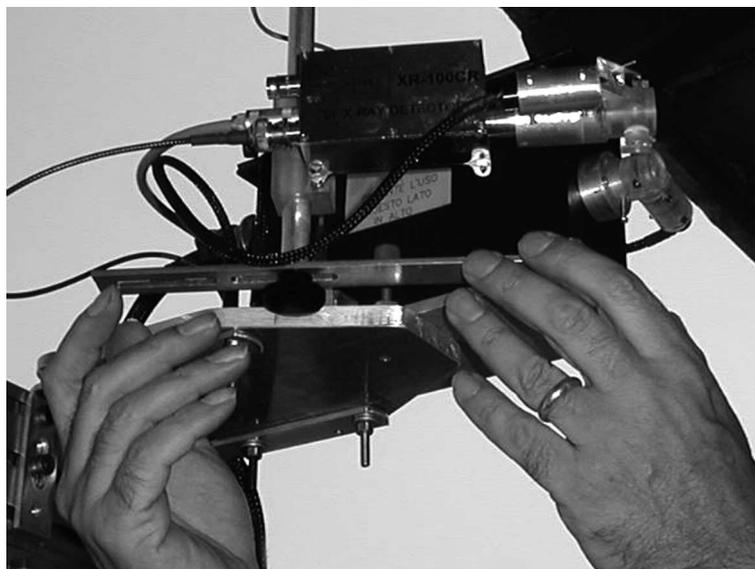


Fig. 1. – Picture of the ED-XRF device, mounted on the mobile arm.

TABLE I. – *Technical data of the instruments used for the portable ED-XRF device.*

X-ray tube:	produced by E.I.S., Rome
Air cooled	
Pd anode	
250 $\mu\text{m}$ thick beryllium window	
Focus: 200x200 $\mu\text{m}^2$	
Maximum voltage: 30 kV	
Maximum current: 0.6 mA	
X-ray detector:	Amptek XR-100CR Si-PIN
Area: 13 $\text{mm}^2$	
Thickness: 300 $\mu\text{m}$	
13 $\mu\text{m}$ thick beryllium window	
Resolution: 280 eV (FWHM) at 5.88 keV (Mn $K_{\alpha}$ line)	
Electronic chain	
Amptek amplifier with 12 $\mu\text{s}$ shaping time	
Amptek multichannel analyser MCA8000A	
Notebook PC	

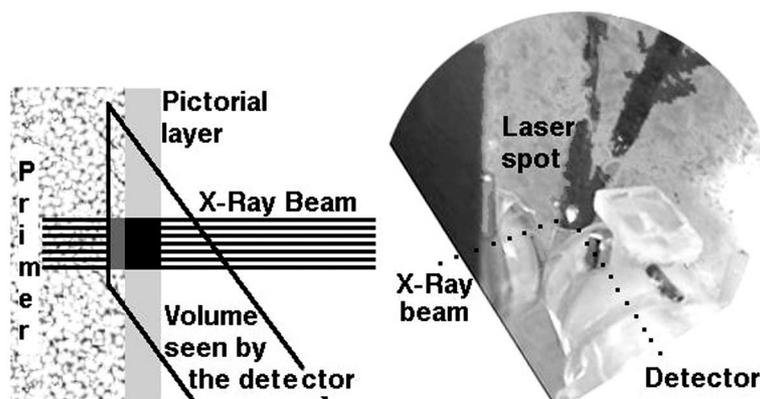


Fig. 2. – Scheme of the device geometry (left) and image of an analysed point, shot with the micro-camera (right).

Many geometrical arrangements were tested in order to reach the best compromise between the maximum peak-to-background ratio of spectrum and the minimum dependence on inaccurate positioning. We changed the incidence angle of the primary X-ray beam and the observation angle of the detector between  $0^\circ$  and  $60^\circ$ . A  $20\ \mu\text{m}$  tungsten wire attached on the surface of a sample was used for this study. From the photon flux emitted from the tungsten wire, we concluded that the best repeatability for positioning the ED-XRF device with respect to the sample was obtained at normal incidence of the exciting X-ray beam. For minimising the air absorption of low-energy X-rays we placed the detector, with its collimator, as close as possible to the irradiated area. This implied that the fluorescence X-rays were collected at  $45^\circ$ . Taking into account the small thickness of the pictorial layer, this choice did not decrease the ratio between the signals collected from the surface and the underlying layers [11].

The aiming is obtained with two laser beams, one coaxial with the X-ray tube and the other with the detector, thus permitting an easy and fast positioning of the sample, without being dependent on the device geometry. A colour micro-camera allows the remote control of the pointing and the acquisition of the image of the analysed spots (fig. 2). The whole device is mounted on a mobile arm with millimetric movements for precise positioning.

The XRF spectra have been deconvoluted with WinAXIL [12], inserting the data about the X-ray source, the detector and the device geometry. These parameters have been measured independently and fixed to reduce the error in the determination of the net areas of peaks from degenerate lines.

Since a mural painting corresponds to a thick and non-homogeneous matrix, we have not conducted a quantitative analysis, but, instead, we calculated the relative percentage of each element, defined as the ratio between the net area of the corresponding peak and the total area of all peaks. The statistical error of the relative percentages is less than 10% for the strongest peaks and does not exceed 30% for the others. Only for potassium the error raises to 50% when it is less than 1% of calcium. It was not possible to resolve the potassium  $K_\alpha$  line from that of calcium when the potassium relative percentage was below 0.1%.



Fig. 3. – Detail of the blue background painting with the red frames and a cup.

### 3. – Samples

For our tests we have chosen two mural paintings located in the Baia Archaeological Complex near Pozzuoli (Naples). The two paintings belong to different Pompeii styles and have undergone different conservation treatments [13].

The first painting (below referred to as the Blue Painting, BP) is a fresco datable to the II style (second half of the I century B.C.). It decorates the wall delimiting the southern side of the sixth terrace of the *Villa dell'Ambulatio*, about 100 m from a road at the same level. Over a dark blue background, some panels, delimited by yellow and red bands, are still visible with candlesticks, cups, and brown figures between them, as shown in fig. 3. These decorations were painted over the background, but the pictorial material has fallen off (pulverised or dissolved), leaving only light traces. On the contrary, the well consolidated blue background, treated with paraloid to preserve its surface, appears compact and resistant, and shows very small crystals.

The second painting, belonging to the IV style (second half of the first century A.D.), has not been restored yet (fig. 4, well described in [13]). It is located in the Venus Complex area, closed to the public, in a room next to the *frigidarium* (the room with the cold water pool) of the small baths, whose function could have been of changing room (*apodyterium*). This painting will be referred to as Painting of the Venus Complex (VP). It has a white background, as smooth and compact as marble, with very small crystals inside. The decorations, painted over the surface, have mostly disappeared, leaving here and there light traces of animals, flowers, branches as well as geometric and architectural elements. Evident traces of calcareous deposits due to the infiltration of water and several efflorescence of saltpetre due to humidity are also present.

ED-XRF measurements have been taken on different colour pigments of both mural paintings and on the plaster layers. In fact, in several areas of the Venus Complex painting, the background layers of the painting, that, starting from the wall, are the



Fig. 4. – The upper part of the painting in the Venus Complex area with a peacock in the centre.

arriccio, the plaster and the primer (*imprimitura*, *i.e.* the surface prepared to receive the colour), were found uncovered and measurements have been taken on them in order to obtain information on the techniques of production. Several pieces of marble, mortar and tuff bricks found in the area have been analysed too. For comparison, in the laboratory, with the same instrumentation, we analysed four pigment samples (blue, light blue, green and white/pink pigments) found in Pompeii and belonging to the Archaeological Museum in Naples, as well as recently prepared slaked lime and plant ash samples. According to Augusti [14], lime water and soap, containing these materials, have been used for spreading the pigments that could be altered in frescoes.

#### 4. – Results and discussion

From the visual inspection of the paintings, the deepest layer of the plaster seems to be made of a thick layer of calcite and sand spread on the wall, followed by 4-5 mm of plaster, in which calcite crystals of up to 2 mm sides can be clearly seen. The primer is as smooth and compact as marble. As Augusti had already evidenced [14,15], the pictorial layer is very thin, a few tenths of a millimetre, being well separated from the plaster.

The relative percentages of the chemical elements found in the plaster, in the materials picked up from the excavations and in the laboratory samples are reported in table II.

The arriccio is a mixture of lime, *i.e.* hydrated calcium oxide with traces of potassium, iron and strontium, and volcanic sand similar to tuff. Tuff is composed by iron, aluminium and potassium silicates with small quantities of many other elements such as titanium, manganese, rubidium, strontium and zirconium, and small traces of copper and zinc. Both the preparation surface of the paintings and the plaster are based on marble or calcite from milled limestone, mixed with slaked lime. Their composition is

TABLE II. – *Relative percentages of the elements measured on the plaster layers of the VP painting and on reference materials.*

Sample	K	Ca	Ti	Mn	Fe	Cu	Zn	Rb	Sr	Zr	K/Ca ×100	Sr/Ca ×100
Arriccio VP	6.2	32.7	0.6	2.1	51.6	0.8	0.5	1.9	1.9	1.3	18.9	5.7
Baia tuff	6.9	8.4	1.6	2.5	74.0	0.9	0.6	1.5	2.2	1.2	81.9	26.6
Primer VP	1.3	96.0			2.2	0.5					1.3	
Plaster VP	1.4	93.2		0.3	3.9	0.7	0.6				1.5	
Slaked lime	1.1	97.8				0.8			0.4		1.1	0.4
Baia marbles	0.7	94.2	0.1	0.6	3.5				0.9		0.8	0.9
Mortar VP	2.6	81.1	0.4	0.6	12.6	0.7	0.6		1.3		3.3	1.6
Plant ash	13.3	59.1		4.6	11.0	3.3	2.4		6.2		22.5	10.5

very similar to the laboratory lime composition, except for the iron percentage, which is closer to that of marble. The analyses show the absence of strontium notwithstanding some authors think it should be widely present because of its high chemical affinity with calcium [16]. The relative percentages of the elements found in the pigments of the Pompeii samples and in the two paintings are reported in table III. They have been divided by colour and the values found in different points have been averaged, whenever data were consistent between themselves within error uncertainties.

The evident traces of sulphur found on the blue painting must be highlighted. This painting has been restored and preserved with a protective varnish, but it is located at the level of a high traffic street from which it is separated by some houses, about 100 m far. Moreover, the painting is located in a humid area, not far from a thermal water spring. Thus sulphur comes from the sulphur dioxide present in the atmosphere either because of the natural emission due to the volcanic activity existing in the area (environmental pollution), or because of human pollution caused by the nearby industrial emissions (fossil fuels) [17].

The white pigments are based on calcareous clays (*paretonium* or *melino*). Another white pigment, made of lead carbonate (*cerussa*), has been found in several mural paintings of the Roman age, but it was rare in Campania. In the particular case of the Baia site, probably the artists were aware that in such a very humid area, rich of thermal springs of volcanic origin, with a large presence of sulphur compounds, *cerussa* would have suffered great alterations, changing to black lead sulphide (PbS) [18].

Regarding the identification of the pigments, it is necessary to point out the effect due to the small thickness of the colours superimposed on the background. Indeed, we should expect an increase of the measured percentages of the elements heavier than copper, whereas only few microns of colour absorb the photons emitted by lighter elements such as calcium and potassium contained in the back layers.

The Pompeii blue pigment is clearly Egyptian blue (also called Pozzuoli blue, since there was a great tradition in preparing this pigment) because of the presence of copper, calcium and iron, and a great variety of trace elements. The blue of the paintings is richer in calcium, strontium, potassium and nickel; therefore it is the same pigment mixed with various media. In particular, potassium and strontium intensities increase with respect to copper, the element characterising this pigment.

The pure green pigment from Pompeii is a clay (green earth), composed of iron and potassium silicates, with traces of several heavy metals. The green pigment found on

the VP painting is probably malachite; the high quantity of calcium and the absence of trace elements suggest that it has been mixed with white clay.

Yellow has a similar composition on both paintings. The iron content is slightly different from the one found in the white pigments; therefore it might be a very diluted mixture of clay with either ochre or an organic (vegetable) pigment.

Several red pigments have been found in the two paintings. In the oldest painting we have a clear example of earth red (Earth of Pozzuoli). The presence of copper and the percentage of iron are due to the small thickness of the colour layer covering the blue background. On the contrary, some reds in the IV style painting contain clear traces of arsenic, indicating the addition of realgar ( $\text{As}_2\text{S}_3$ ) to the red earth or a different origin of the pigment. The pigment of a black flower turned out to be based on mercury, a clear example of cinnabar ( $\text{HgS}$ ) that has undergone the transition to the black phase.

The Pompeii pink pigment is odd, since it has the highest percentage of calcium with respect to the other Pompeii pure pigment samples. In addition it shows a higher content of potassium and strontium with respect to calcium, with significant traces of titanium and zirconium. It could have been a pigment derived from red earth or ochre mixed with white clay and other compounds to obtain the desired colour shade.

A few observations are due on the media employed. We have noticed that in all the analysed points there is a significant increase of the calcium percentage with respect to the pure pigments, which depends only in part on the calcium present in the preparatory layers. In addition, also strontium and potassium percentages increase with respect to the element characterising the pigment. Their ratios over calcium are almost constant in the spots measured on the pictorial layer, whereas it becomes negligible in the other points lacking of the pictorial layer. Thus we think that the pigments have been diluted with lime and that other substances rich of potassium and strontium have been added before spreading the painting over the mortar with the purpose of neutralising the causticity of lime. We note in particular that, in the case of cinnabar red, well known by the ancient Romans for turning easily to the black phase, the ratio between potassium (strontium) and calcium is the highest.

## 5. – Conclusions

A portable ED-XRF device has been set up assembling commercial instrumentation. It has been tested on two mural paintings of Roman age, but it can be employed on every work of art. The measurements on the two paintings have allowed us to evaluate its performance, mainly the goodness of geometry, focusing and pointing systems. Concerning the pigments used, the absence of lead-based colours have been highlighted. The whites are clay-based pigments and the reds are made of red earth and realgar. Only with the ED-XRF analysis it has been possible to discover that a black flower actually was red at the origin, painted using cinnabar.

The two paintings contain different types of pigments: the first one is made of natural earth-based pigments, except for the cerulean blue background from Pozzuoli; the second one shows mineral pigments, mostly in reds. The blue painting shows also traces of sulphur and chlorine (not reported in the table for compactness reasons), due to the exposition to polluting environments. Even though from different ages, the techniques of production of the two paintings are very similar. The plaster is made of several layers: the arriccio, containing lime and sand from Pozzuoli, followed by a plaster made of lime and milled limestone. A superficial enrichment of strontium and potassium due to the media used to lay the colour can be noticed. The first element is due to the use of clay

TABLE III. – *Relative percentages of the elements present in the pigments of the Pompeii samples and in the colours of the two paintings. The last two columns give the ratios between the intensities of K (Ca) and the element characterising each pigment (cha). The latter is indicated with bold characters in the relative percentages table.*

Colour	Sample	S	K	Ca	Cr	Fe	Ni	Cu	As	Hg	Sr	K/Ca ×100	Sr/Ca ×100	K/cha ×100	Sr/cha ×100	Pigment
Blue	Pompeii n.104		0.3	5.7		5.4		<b>87.6</b>				5.3		0.3		Pozzuoli blue
Blue	Pompeii n.105		0.2	3.2		4.3		<b>91.6</b>				6.3		0.2		Pozzuoli blue
Pink	Pompeii n.109		1.3	18.7		<b>72.1</b>		1.0			2.2	7.0	11.8	1.8	3.1	Red earth
Green	Pompeii n.113		2.5	2.2	1.6	<b>86.8</b>	2.2	3.0				1.1		2.9		Creta Viridis
Blue	BP - background	0.8	0.7	34.1		4.0	0.6	<b>57.6</b>			1.3	2.1	3.8	1.2	2.3	Pozzuoli blue
Blue	VP - peacock		0.9	48.2		7.2	0.6	<b>40.1</b>			2.8	1.9	5.8	2.2	7.0	Pozzuoli blue
Green	VP - decoration		1.6	78.0		2.9		<b>15.2</b>			2.3	2.1	2.9	10.5	15.1	Armenium
Red	BP - figure	0.2	1.0	51.5		<b>19.4</b>		23.1			4.0	1.9	7.8	5.2	20.6	Earth of Pozzuoli
Red	VP - band		0.8	66.9		<b>27.9</b>		1.0	<b>0.7</b>		2.1	1.2	3.1	2.9	7.5	Earth of Pozzuoli
Red	VP - decoration		0.3	30.5		<b>66.5</b>		0.3	<b>1.5</b>		0.6	1.0	2.0	0.4	0.9	Earth of Pozzuoli
Yellow	BP - band	1.4	0.9	<b>88.4</b>		5.7		0.9			2.3	1.0	2.6	1.0	2.6	Ochre or organic
Yellow	VP - band		1.9	<b>90.9</b>		4.3		0.5			2.3	2.1	2.5	2.1	2.5	Ochre or organic
Black(*)	VP - flower		3.9	66.2		<b>22.0</b>		0.9		<b>2.9</b>	2.8	5.9	4.2	17.7	12.7	Earth and Cinnabar
White	VP - background		0.4	<b>94.8</b>		3.8					1.0	0.4	1.1	0.4	1.1	Paretonio or Melino

(\*) Dark, almost black, because of the chemical alteration of cinnabar (HgS).

and/or gypsum, the second one, present in a selective way, could have been originated by a substance, such as soap, suited to neutralise the lime causticity, according to what Augusti [14] asserted about the Pompeii paintings. Indeed, none of the compounds mentioned in the ancient literature (Plinio, Vitruvio) [19,20] show a quantity of potassium that can justify the amount found in the examined colours.

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