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The Contribution Of The LNS Portable PIXE System For The Examination Of Gold Preparations In The Miniatures Of The 492 Code (Pontificale) Preserved At The Museo Diocesano In Salerno (Italy)

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Abstract. The gold preparations of the Salerno 492 code were examined by means of the LNS portable PIXE-alpha spectrometer. Complementary XRF and micro-Raman techniques were also used. Quantitative data enable to establish the composition of the various gold preparations.

Keywords: PIXE, PORTABLE, GOLD PREPARATIONS

INTRODUCTION

The 492 code of the Museo Diocesano of Salerno is dated back to a period from the end of XIII century and the incoming of the XIV one. It has been submitted to an important and innovative restoration and conservation treatment at the Istituto Centrale per la Patologia del Libro (ICPL) in Rome. It consists of 349 parchment sheets each having dimensions 400 x 285 x 80 mm.

The miniatures are of excellent quality and the pigments (lead white, minium, lapis-lazuli, mosaic gold, yellow-ochre, earths, etc.) are often in poor state of conservation. Gold is present as "foil": many layers of thin gold-leafs are applied on the *asisum* (the preparation for gold illuminations).

The manuscript has not been completed by the miniaturists; in some cases only the preliminary design is present, in other cases the preparation is not covered by the gold-foil. The above circumstances give the unique opportunity to investigate the different techniques used by the miniaturists and in particular the composition of the gold preparations and their comparison with the medieval recipes.

Due to the uniqueness of the masterpiece only non destructive analytical techniques must be used; also, portable apparatus are required. In fact, the Pontificale cannot be removed from the restoration site [1].

In the present work we confine our attention to the analytical problems raising by the n.d. characterization of the gold preparations. These problems can be defined as follow:

i) *Quantitative (or semi-quantitative) analysis of heavy and light elements are requested:* as it is known from ancient documents [2,3] the gold preparations are essentially made of bolo (an aluminum silicate containing more or less iron), gypsum (calcium sulfate hydrate) and, in some case, lead-white. It must be observed that different miniaturists used a mixture of various components each with different proportions. *Then, to distinguish between the different "hands" it is important to obtain quantitative or semi quantitative analytical results of light and heavy elements.*

ii) *Gold preparations are in general few microns thin.* They are carefully spread on the parchment into the surface delimited by the preliminary design. Gold-foils are applied on the preparation before the pigments.

PIXE technique seems to be the most appropriate. In fact: the analyzed thickness is a few microns at low incident energy; light elements are well detected; quantitative analysis can be performed under reasonable hypothesis; portable PIXE systems are nowadays available.

EXPERIMENTAL

The LNS/INFN portable PIXE-alpha spectrometer (see Fig.1) has been described elsewhere [4].

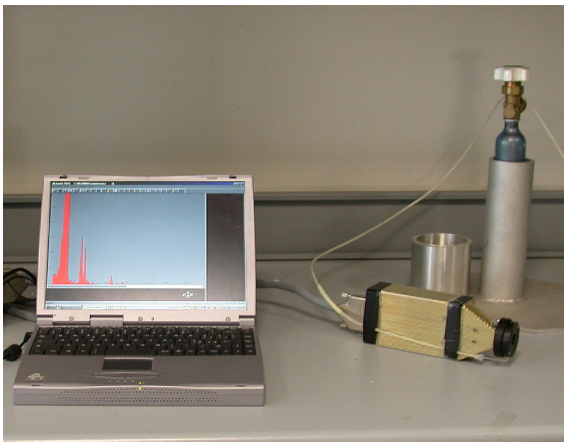

FIGURE 1. The portable PIXE-α system

It consists of a ^{210}Po alpha source, with activity less than 37 MBq, coupled to a Si-drift detector and to a Helium flux. In the PIXE-alpha spectrometer the use of the Helium flux increases considerably the detection efficiency of Na, Al, Mg and Si, while at the same time eliminates the interfering Ar-K lines from the measured spectra. The analytical capabilities of the spectrometer extend from Na to Zn via the detection of their K lines, as well as to heavier elements such as Sn, Ag, Au and Pb via the detection of their L or M emission lines. Thanks to its very small dimensions, and low weight, the system can be easily transported in the place in which the object is collected and displayed (museum, archaeological site). Typical measurements, performed by placing the samples in contact with the source (spot diameter is 7 mm), require a measuring time of about 30 min, in order to obtain satisfactory statistics for most of the elements. The small range of the alpha particles, penetrating only into the first 5-10 μm of the analyzed surface, allows the technique to be characterized as surface sensitive.

Quantification of the PIXE-alpha spectra is performed by means of the GUPIX 2003 code [5]. The accuracy of the PIXE-alpha analysis was evaluated by measuring the international geological standard SCO-1. The minimum detection limits range from 0.25% for Na_2O up to 1.3 % for Fe_2O_3, respectively.

The analyzed depth of 5 Mev alpha particles in a light matrix is about 5-10 microns which is the order of magnitude of the gold preparations.

In some cases an ambiguity can arise in the PIXE analysis concerning those elements whose characteristic X-rays lie in the energy region from 2 to 3 keV due to the possible presence of S (K-line), Au (L-line), Pb (M-line), Hg (M-line). So, it is useful to associate to PIXE analytical method the XRF (X-Ray Fluorescence) one, sensitive to L-lines of the heavy elements, in order to qualitatively indicate the presence or absence of one or more of the above heavy elements that can interfere with sulfur. They will be included or excluded from the analytical procedures in much cases simplifying the analysis. The new stability controlled XRF spectrometer [6] has been used.

Also, the micro-Raman installed at ICPL [7] has shown its invaluable contribution in those cases in which the fluorescence effect has been negligible.

RESULTS

In the present section we report some representative examples of the analyzed points.

Fig.2 shows two sheets (C105v, C106r) of the Salerno Pontificale under study. It is impressive to notice how the gold was applied in the miniatures. In some cases the application has been completed; however in other cases it is possible to evidence that only the preparations are placed on the parchment. These parts represent an interesting case very suitable to perform analytical investigations.

We focused our analysis to the preparation indicated by the arrow.

The PIXE spectrum is shown in fig.3. Light elements as Al, Si, S, Ca and Fe are present in the spectrum

The PIXE analysis is reported in the line 1 of Table 1. The important content of Al, Si and Fe can be related to the presence of a *bolo* (an aluminum silicate containing Fe), which is one of the more used components of the gold preparations [2,3]. In the present case it is mixed with *gypsum* ($CaSO_4 \cdot 2H_2O$) as can be deduced from the presence of S and Ca.The same conclusions can be drown for the miniatures of C114r and C108r sheets (cf. figures 4 and 5).

TABLE 1. Red preparations

	Quantitative Data in % weight - PIXE-alfa							Counts - XRF			OTHERS (n.q.)	Preparation
SAMPLE	Al	Si	S	Ca	Fe	Au	Pb	Fe	Au	Pb		
C106r (Pont 35)	3.5±0.2	3.8±0.1	11.8±4	17.1±3.0	4.1±0.6			50			Na, Cl, Ti	gypsum+bolo
C114r (Pont 42)	2.9±0.2	2.6±0.2	6.6±0.3	9.8±0.4	2.1±0.4	33.9±1		82	134		Cl, Ti	gypsum+bolo+Au
C108r (Pont 37)	3.0±0.3	3.8±0.4	8.9±0.5	16.3±1.0	2.8±1.1		4.3±1.5	77	122	traces	P, Ni, K	gypsum + bolo + white lead+Au (XRF)

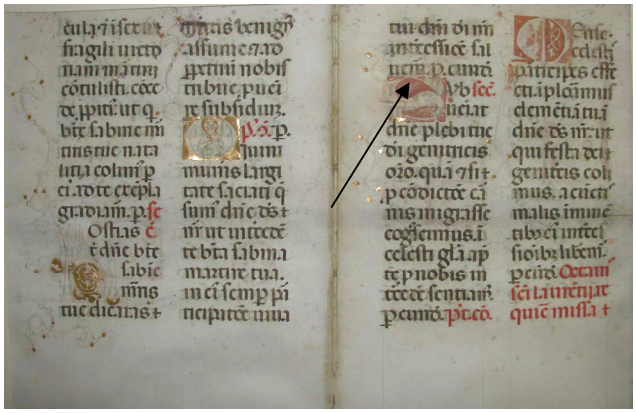

FIGURE 2. Sheet C105v & C106r of the Pontificale under study. The arrow indicates the measurement point (C106r).

Table 2 shows the PIXE results of a different set of samples: white preparations are evident together with a layer of gold. This is the case of miniatures on C76r (Fig. 6), C45v and C43v (Fig.7) for which the results suggests the presence of gypsum and white lead. The ratio of their concentration determination is not affected by the thin gold layer presence.

We note that the ratio between Ca and S is rather consistent with the stoichiometric one of the gypsum $CaSO_4 \cdot 2H_2O$.

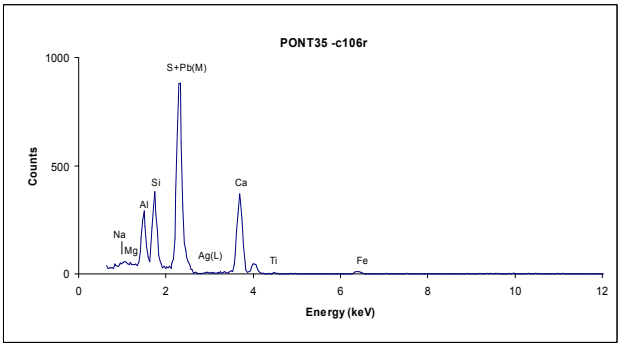

FIGURE 3. PIXE-alpha spectrum of the gold preparation indicated in Fig. 2

FIGURE 4. Sheet C114r of the Pontificale under study. The arrow indicates the measurement point. The PIXE analysis is reported in the line 2 of table1. Gold contaminations are present.

FIGURE 5. Sheet C108r of the Pontificale under study. The arrow indicates the measurement point. The PIXE analysis is reported in the line 3 of Table 1.

Some samples have been analysed using the micro Raman technique. Fig. 8 reports Raman spectra of gypsum and white lead. The spectra have been collected with Argon ion LASER (excitation λ=514.5 nm). The typical peaks at 1005 cm^{-1} for gypsum and 1050 cm^{-1} for white lead are easily distinguishable also when they are used in mixture.

TABLE 2. White preparations

	Quantitative Data in % weight - PIXE-alfa									Counts - XRF		Preparation
SAMPLE	**Na**	**Al**	**Si**	**S**	**Cl**	**K**	**Ca**	**Au**	**Pb**	**Au**	**Pb**	
C76r (Pont 28)	n.q.	n.q.	0.9±0.2	9.0±0.6		n.q.	12.3±0.7	23.7±1.0	5.0±2.0	180	93	gypsum + white lead + Au
C45v (Pont 25)			0.8±0.1	7.7±0.3		n.q.	14.6±1.0	23.8±1.0	7.5±0.5	362	traces	gypsum + white lead +Au
C43v (Pont 14)	2.2±0.8		0.2±0.1	9.4±0.4	n.q.		11.6±0.3	33.2±0.7	4,3±1.3	192	58	gypsum + white lead + Au

FIGURE 6. Sheet C76r of the Pontificale under study. The arrow indicates the measurement point. The PIXE analysis is reported in the line 1 of Table2.

FIGURE 7. Sheet C43v of the Pontificale under study. The arrow indicates the measurement point. The PIXE analysis is reported in the line 3 of Table 2.

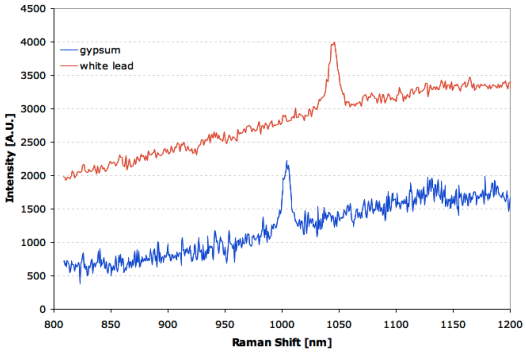

FIGURE 8. Raman spectra of gypsum and white lead. λ=514.5 nm

CONCLUSIONS

We have shown that the portable PIXE-α gives invaluable contribution to the characterization of gold preparations due to its characteristic (portability, well definite analytical depth, possibility of quantitative analysis). XRF and microRaman are precious complementary techniques.

In the course of our work a total of 9 points was analysed: 3 different preparations were identified. Two of them of red/brown color consist of gypsum mixed with two different kinds of bolo; the third one of white color consists of gypsum mixed with white lead.

ACKNOWLEDGMENT

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REFERENCES

[1] M. Bicchieri, M. Nardone, G. Pappalardo, L. Pappalardo, F.P. Romano, P.A. Russo, A. Sodo, *Analisi non distruttive PIXE-alfa, XRF e μ-Raman* in Il Codice "incompiuto" del Museo Diocesano di Salerno (Pontifical 492), C. Cassetti Barch R. Carrarini eds., Lobri e Carte, Gangemi, Roma, 2006, pp. 86-93

[2] De Arte Illuminandi, Ed. F. Brunello, Ricetta VII, Neri Pozza, Vicenza (1975)

[3] C. Cennini, Il libro dell'Arte, Ed. F. Brunello, - Cap. CLIX, Neri Pozza, Vicenza (1976)

[4] L. Pappalardo, F.P. Romano, S. Garraffo, J. de Sanoit, C. Marchetta, G. Pappalardo, Archaeometry 45 (2003) 333-339

[5] T.L. Hopman, Z. Nejedly, J.A. Maxwell, W.J.Campbell, Nucl. Instr. And Meth.B 189 (2002) 138

[6] F.P. Romano, G. Calvi, E. Furia, S. Garraffo, C. Marchetta, G. Pappalardo, L. Pappalardo, F. Rizzo, A. Rovelli, X-Ray Spectrometry, 34, (2005), 135-139

[7] M. Bicchieri, M. Nardone, A. Sodo, J. Cultural Heritage 1(2000), S277-S279.