



Non-destructive characterization of fifty various species of pigments of archaeological and artistic interest by using the portable X-ray diffraction system of the LANDIS laboratory of Catania (Italy)

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ABSTRACT

In recent years a portable XRD system with high angular resolution and rapid measurement time was realized at the LANDIS laboratory of the LNS-INFN and IBAM-CNR of Catania (Italy) for application in the cultural heritage field. The system was previously used for the characterization of some pigments present in ancient frescoes. The main task of this work is to show the possibility of using the above portable diffractometer in the identification of a large variety of pigments commonly used to realize archaeological and artistic masterpieces.

50 reference standards of pigments with a known mineralogical composition were prepared and measured; analytical results evidenced both the advantages and the limitations of using such a system in the analysis of different typologies of pigments and allowed to realize a raw database to be used during the characterization of real samples.

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1. Introduction

It is well known that the XRD technique can be used for the mineralogical characterization of materials in the cultural heritage field.

Generally the XRD technique is applied with non-transportable instruments, so limiting its field of application only to small dimension objects or requiring a destructive sampling in order to analyze artifacts which cannot be transferred to analysis laboratories.

In the last years many efforts have been dedicated to the development of portable systems, even if some limitations in terms of angular resolution or measurement time are often observed [1–3].

In 2006 at the LANDIS laboratory of the LNS-INFN and IBAM-CNR of Catania a portable XRD system of high angular resolution was installed to be applied in the cultural heritage field [3]. It was realized by upgrading a commercial goniometric diffractometer with a microfocus X-ray tube coupled to a polycapillary optics of small divergence. As further upgrade a new digital acquisition electronics and a new control software were recently installed on the system in order to perform diffraction measurements in shorter time (less than 1 h).

The system was used for the mineralogical characterization of a few archaeological fragments of frescoes dated back to the Roman period [3,4]. Moreover, by combining the portable PIXE-alpha and XRD tech-

niques developed at LANDIS laboratory, an absolute quantitative analysis of the pigments (and their mixtures) has been obtained [4,5].

In the present work the upgraded version of the XRD system is used for the non-destructive mineralogical characterization of a large variety of pigments usually present in ancient artifacts.

50 reference standards were prepared at LANDIS laboratory and analyzed by the XRD apparatus [6]. In some cases XRD measurements were combined with the ones performed by using the portable PIXE-alpha system. In fact the preliminary knowledge of the elemental composition of sample being analyzed allows restricting the search in XRD spectra only to the mineralogical phases containing the elements evidenced by the PIXE measurements. This approach allows the analysis of diffractograms even if the diffraction peaks are present with low intensities due to a small quantity of material or to a mineral not very sensitive to the diffraction analysis at the experimental set-up of the XRD system.

Results allowed to evidence the capabilities and the limits of the portable XRD system in analysis of pigments and helped to realize a raw database to be used in the analysis of real samples.

2. Experimental

The new version of the portable XRD system [3] was realized starting from a commercial goniometric apparatus realized by the Italian ASSING company and installed at LANDIS laboratory for *in-situ* applications in the cultural heritage field.

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The ASSING system evidenced some important analytical capabilities: the sample can be positioned outside the goniometric mechanics allowing its use for non-destructive measurements of non-movable artifacts (for example wall paintings or frescoes); it makes possible the simultaneous measurements by using both XRD and XRF techniques on the same area of the sample; the selection of the X-rays energy used to perform the diffraction on the samples is obtained by a digital filter that operates in the MCA analyzer of the detector; finally it presents compact dimensions and low weight and it is easily transportable in-situ.

However the ASSING system presented some analytical limitations: it was necessary to operate long measurements (about 3 h) to get sufficient statistics in diffractograms and it presented a low angular resolution reducing the capabilities to resolve peaks with close diffraction angles.

The commercial version of the XRD system was upgraded by using a new X-ray source realized by the German IFG company. It consists of a 10 W microfocus X-ray tube with a Fe anode coupled to a polycapillary semi-lens optics. The use of the polycapillary optics allows catching most of the X-rays intensity produced in the 50 μm focal spot size of the Fe anode and, thanks to the semi-lens geometry, to obtain a parallel X-ray beam with a small divergence (only 0.26°) at the output of the source. The final beam spot diameter is 600 μm .

Finally a 25 mm² Si-PIN detector produced by the AMPTEK Company is used to detect the X-rays diffracted from the samples.

In order to limit the dimensions of the investigated area at the sample position (about 20 cm from the source output), both the polycapillary and the Si-PIN detector are collimated by two slits with

1 mm aperture. The new experimental set-up of XRD system was tested by performing measurements on a calcite standard; results were compared with those obtained by using the previous version of the system operating at the same conditions. Diffractograms were collected in the θ angular range from 12 to 67° with a step size of 0.05° and acquisition time/step of 5 s.

Fig. 1 shows a comparison between the diffractogram of calcite obtained by the new version of the system and the one obtained by the original diffractometer: the measured angular resolution at the (104) peak of calcite ($I_{\%} = 100$) at $\theta = 18.62^\circ$ was 0.12 and 0.2° for measurements performed respectively with the new version of the system and with the old version showing an improvement of 40%. These data have been obtained by fitting the spectra with a Gaussian

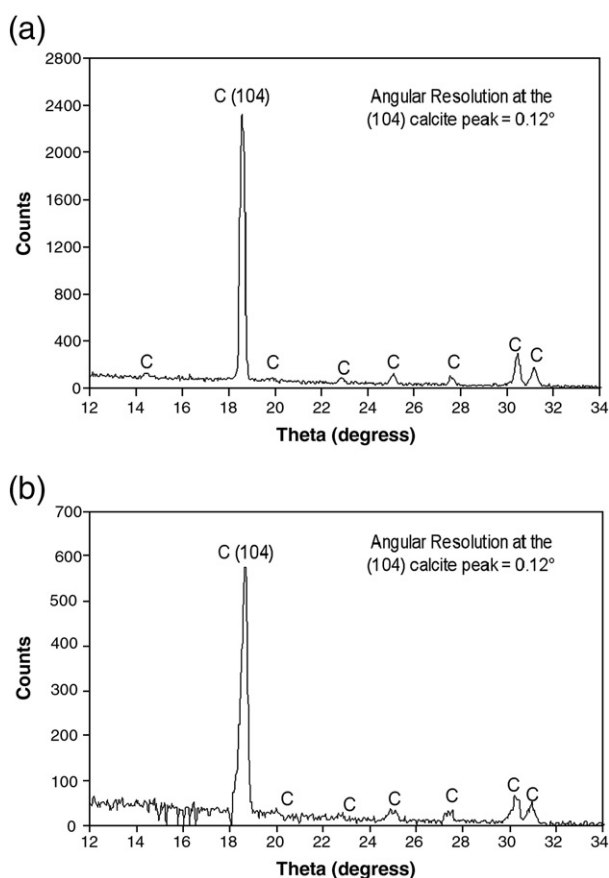


Fig. 1. Comparison between the calcite spectrum (a) obtained with the new version of the XRD system and (b) the one measured with the original apparatus. Improvements in terms of angular resolution and intensity are evident.

Table 1

The standards prepared for the analysis with the LANDIS portable XRD system. Both pellets and dummy frescoes are listed.

	%	Chemical formula
Pellets		
Yellow ochre	100	FeO(OH) + clays
Yellow ochre + calcite	50–50	FeO(OH) + clays + CaCO ₃
Red ochre + calcite	50–50	Fe ₂ O ₃ + clays + CaCO ₃
Sienna earth + calcite	50–50	FeO(OH) + manganese oxides + clays + CaCO ₃
Sienna earth	100	FeO(OH) + manganese oxides + clays
Umber earth	100	FeO(OH) + manganese oxides + clays
Green earth + calcite	50–50	(K,Na)(Fe ^{III} ,Al,Mg) ₂ (Si,Al)O ₁₀ (OH) ₂ + CaCO ₃
Green earth	100	(K,Na)(Fe ^{III} ,Al,Mg) ₂ (Si,Al)O ₁₀ (OH) ₂
Verdaccio + calcite	50–50	+ CaCO ₃
Azurite + calcite	50–50	Cu ₃ (CO ₃) ₂ (OH) ₂ + CaCO ₃
Minium + calcite	50–50	Pb ₃ O ₄ + CaCO ₃
Cinnabar + calcite	50–50	HgS + CaCO ₃
Litharge + calcite	50–50	PbO + CaCO ₃
Titanium white	100	TiO ₂
Calcite	100	CaCO ₃
Gypsum	100	CaSO ₄
Quartz	100	SiO ₂
Quartz + gypsum	20–80, 80–20, 50–50	SiO ₂ + CaSO ₄
Calc + quartz + gypsum	50–25–25	CaCO ₃ + SiO ₂ + CaSO ₄
Dummy frescoes		
1. Frescoes		
Malachite	100	Cu ₂ (CO ₃)(OH) ₂
Red ochre	100	Fe ₂ O ₃ + clays
Yellow ochre	100	FeO(OH) + clays
Sienna earth	100	FeO(OH) + manganese oxides + clays
Umber earth	100	FeO(OH) + manganese oxides + clays
Green earth	100	(K,Na)(Fe ^{III} ,Al,Mg) ₂ (Si,Al)O ₁₀ (OH) ₂
Azurite	100	Cu ₃ (CO ₃) ₂ (OH) ₂
Cinnabar	100	HgS
Green earth + orpiment	58–42	(K,Na)(Fe ^{III} ,Al,Mg) ₂ (Si,Al)O ₁₀ (OH) ₂ + As ₂ S ₃
Red ochre + cinnabar	20–80	Fe ₂ O ₃ + HgS
Red ochre + Sienna earth + yellow ochre	29–30.5–40.5	Fe ₂ O ₃ + FeO(OH) + manganese oxides + FeO(OH) + clays
Green earth + umber earth + cinnabar	42.4–6.6–51	(K,Na)(Fe ^{III} ,Al,Mg) ₂ (Si,Al)O ₁₀ (OH) ₂ + FeO(OH) + manganese oxides + HgS
2. Tempera		
Azurite + velat. ultramarine	100	Cu ₃ (CO ₃) ₂ (OH) ₂
Minium	100	Pb ₃ O ₄
Lead-tin yellow	100	Pb ₂ SnO ₄
Original cinnabar	100	HgS
Mineral cinnabar	100	HgS
Verderame	100	(CH ₃ COO) ₂ Cu
Litharge	100	PbO
Caeruleum	100	CoO * nSnO ₂ + CoSn(OH) ₆

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