The diagnostic analysis for the study and restoration of the mosaic fragment with an Angel from Giotto's *Navicella*

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Riassunto

Il frammento musivo con Angelo, oggetto di questo lavoro, è oggi conservato nelle Grotte Vaticane e proviene dalla *Navicella*, il grande mosaico di Giotto posto nell'atrio della Basilica di S. Pietro. Nell'ambito delle celebrazioni per il VII centenario della morte di Bonifacio VIII il frammento musivo è stato sottoposto a restauro; in questa occasione è stata effettuata una campagna di indagini diagnostiche, allo scopo di conoscere i materiali e la tecnica esecutiva.

Il frammento è stato analizzato adottando un approccio analitico ad ampio spettro. Le tessere musive e le malte sono state investigate mediante una campagna fotografica in luce visibile, all'infrarosso in falsi colori (IRC) e in fluorescenza indotta da radiazione UV e attraverso acquisizioni con videomicroscopio; sono state inoltre condotte analisi XRF sulle paste vitree. I pigmenti e le malte utilizzati nelle integrazioni effettuate dai precedenti restauri sono stati inoltre indagati con microscopio polarizzatore (MP) su sezioni lucide e sottili e analisi FTIR dei leganti.

Parole chiave: mosaico, paste vitree, XRF, FTIR, microscopia.

Abstract

The wall mosaic fragment with an angel, subject of this paper, is displayed in the Vatican Grottoes and it comes from the *Navicella*, a large mosaic by Giotto formerly in the hall of the medieval S. Peter Basilica. For the celebrations of the VII centenary of the death of Boniface VIII the mosaic fragment has been restored; in this occasion a diagnostic campaign of analysis was executed with the aim to study the materials and the executive techniques.

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The mosaic fragment was investigated through a wide analytical approach. *Tesserae* and mortars have been investigated through visible, false colour infrared (IRC) and ultraviolet (UV) fluorescence photography and video microscope acquisitions; moreover, XRF has been performed on the glass pastes. Pigments and mortars used in the integrations of the previous restorations have been also investigated through polarizing microscope (PM) and FTIR analysis of the binding materials.

Keywords: mosaic, glass pastes, XRF, FTIR, microscopy.

Introduction

In the hall of the medieval S. Peter Basilica in Rome there was the large mosaic of the *Navicella*, by Giotto (Andaloro, 2009). Due to the reconstruction of the Basilica the work has been transported many times; actually only two fragments survived from it. One of them has been object of the present research (Fig. 1); it was discovered in 1924 under another mosaic that showed an angel, executed in 1728. The original fragment and that one from its 18th century 'cover' are now exposed in the Vatican Grottoes.

Since its re-discovery, the mosaic with an angel underwent several restorations (in 1924, 1950 and about in 1975) that altered its iconography and its structure (Pogliani, 2009), especially the last intervention realized on the mosaic *tesserae* surface between 1975 and 1980. For this reason, the 'Boniface VIII Committee', institution founded by Ministry for Italian Arts and Culture, promoted and funded a restoration intervention of the mosaic. A multidisciplinary team composed by historians of art, conservators, chemists, physicists, belonging to the Faculty of Conservation of Cultural Heritage of Viterbo and the ENEA (Italian Institute for New Technologies, Energy and the Environment) provided this restoration with a wide support of research and investigation, working in synergy with the restorers in order to plan the most appropriate intervention. The preliminary results of this research were related to the one day conference *L'angelo dalla Navicella nelle Grotte Vaticane. Autopsia di un frammento*, organized by Maria Andaloro and Silvia Maddalo, that took place on 23rd June 2006 at University of Viterbo.

Materials and Methods

The study of the original matter of the mosaic had been possible exclusively by means of non-invasive techniques (video microscope, photography and XRF), whereas not original pigments and mortars due to the past

Fig. 1 – Mosaic fragment before the restoration. Photograph: Domenico Ventura ©.

restorations were examined also through laboratory analyses carried out on micro-samples taken from the artefact.

UV fluorescence photographs were taken using a 6x6 Hasselblad camera and 4x160 Watt Philips MLW UV lamps positioned at 45° as regards the surface to be examined, on a Fujicolor NPH 160 W daylight colour film. In front of the camera lens was placed a Kodak 2E Wratten gelatine filter. The IRC photographs were taken with the following equipment and according to the following conditions: Nikon camera F3 on Kodak Ektachrome, Infrared film and Kodak n. 12 and Wratten gelatine filter, from time to time, coupled with Kodak CC50 Cyan, CC30 Magenta and CC20 Cyan filters. The lighting system was made up of 2x500 Watt High component IR Photolyte lamps.

The UV and IRC photographs of the mosaic fragment were taken before and after the restoration intervention.

The glass pastes were investigated using an X-Ray fluorescence spectrometer equipped with a Gilardoni CPX-M160 X-ray generator and a EG&G ORTEC Ge (hp) detector with 195 eV resolution at 5.9 keV. The distance between the target and the detector was 6.5 cm; the measurement time was 180 s. The generator operates at 60 kV/4.0mA and 20 kV/ 4.0mA. The last condition was employed to reveal the elements that emit less X-rays energy.

The video microscope acquisitions were carried out by a Keyence instrument equipped with 25-175x zoom lens.

The restoration pigments, mounted in Canada balsam, and the cross and thin sections of mortars, embedded in polyester resin, were examined with a Zeiss Axioskop polarizing microscope at 2.5-40x magnification in incident and transmitted visible and UV lights. Photomicrographs were taken with the digital Zeiss AxioCam MR.

FTIR (Fourier Transform Infrared) and μFTIR analyses were performed by a Nicolet Avatar 360 spectrophotometer equipped with a DTGS detector and connected to a Centaurμs microscope equipped with a MCT detector. The spectra were collected in diffuse reflection modality. For each spectrum 200 consecutive scans were recorded with a resolution of 4 cm^{-1}. As background, the spectrum of the KBr powder was used.

Results and discussion

Ultra-violet fluorescence photography

Through ultra-violet photography surface damage and restoration materials received greater clarity. The following observation were obtained:

– the presence of a diffuse light-blue fluorescence due to ancient restoration materials;
– a localized bright red fluorescence due to the use of a red lake for the false mosaic integration in the red areas rounding the Angel. This red lake was identified thanks to the polarizing microscope examination of the thin section obtained from a sample taken from this area (Fig. 2);
– the presence of white spots localized in the integration stuccos inside the clypeus and on the face of the angel, probably due to oils.

Infrared photography

Owing to the characteristic absorption of certain pigments in the infrared area of the electromagnetic spectrum, in many cases it became possible to make hypothesis on the pigment composition. Nevertheless the precise identification of the pigments used for the false mosaic integration and for the more recent paintings was realized through the polarizing microscope

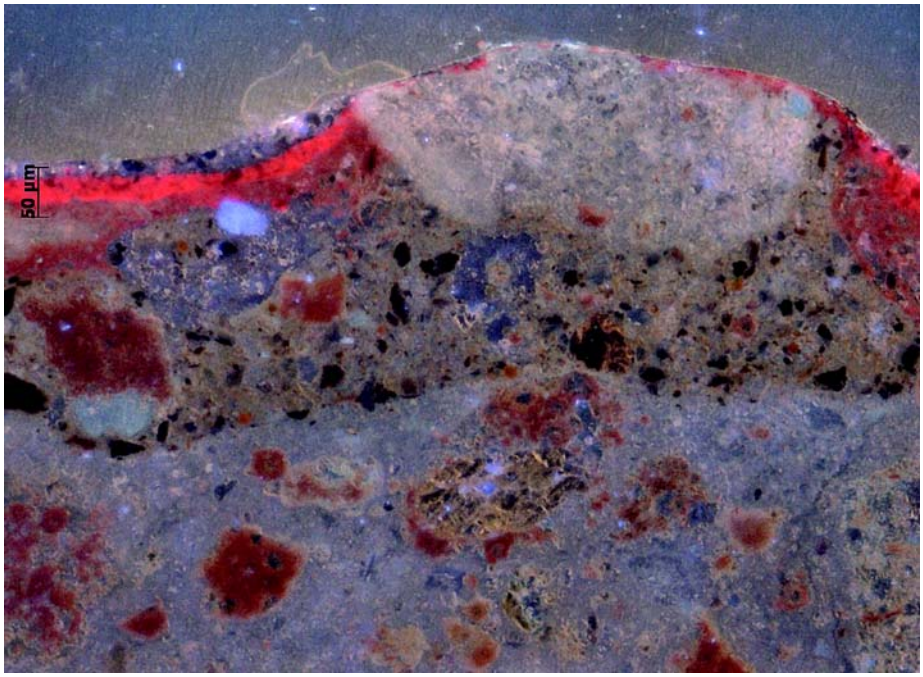

Fig. 2 – Thin section of a micro sample taken from the red area on the right of the mosaic (red false mosaic reintegration).

observation on samples. The results are reported in Table 1. For example the blue false mosaic integration (about 1950) was painted with cobalt blue, characterised by mid-to deep blue isotropic particles in the range of 10-20 µm (Roy, 2007), whereas for the blue additional touches, realized between 1975 and 1980 on the mosaic *tesserae* surface, was used artificial ultramarine characterised by pure blue isotropic rounded particles of regular size and shape (about 5 µm) (Plesters, 1993). Cobalt blue and artificial ultramarine have been distinguished thanks to their slightly different infrared false colours but particularly for different optical characteristics of their particles observed under the polarizing microscope (Fig. 3).

We also tried to make a comparison between the IR colours of the *tesserae* and their elemental composition obtained with the XRF analysis, but it was very difficult to find any correlation. There are only few references about the use of this photographic technique to the study of mosaic *tesserae* so we are trying to test it, but further experimental plans will be necessary (Aldovrandi et al., 1996; Fiori et al., 2003). The aim of this comparison was to find a correlation between the composition of the *tesserae* and their infrared false colours, in order to make possible the use of this simple and inexpensive photographic technique to the study of the mosaics.

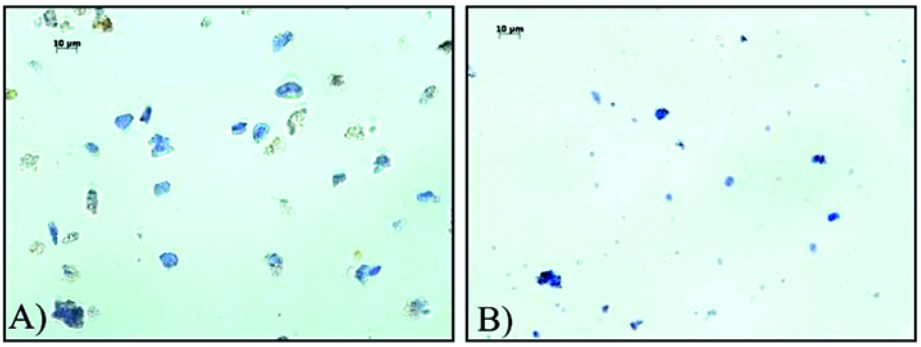

Fig. 3 – Photomicrographs of the blue pigments. A) 1950 false mosaic integration, cobalt blue; B) 1975-1980 additional touches on the mosaic surface, artificial ultramarine. Transmitted light, N//, ob. 40x.

Tab. 1 – Comparison between the visible and IR false colours of the pigments and the microscope observation.

Visible colour	*IR false colour*	*Microscope observation*	*Identified pigment*
Blue (about 1975)	Dark red	Pure blue isotropic rounded particles of regular size and shape (about 5 μm)	Artificial ultramarine
Green (about 1975)	Light violet	Weakly translucent, rounded and sub-rounded particles with smooth surface (about 5-10 μm).	Phthalocyanine green
White (about 1975)	Grey	Very fine particles (<1μm) with low birefringence	Zinc white
Orange (about 1975)	Light Orange	Fine birefringent particles of variable size and little particles with moderate birefringence and blue-green interference colours.	Red ochre and lead red
Blue (1950)	Pink-red	Mid-to deep blue isotropic particles in the range of 10-20 μm	Cobalt blue
Yellow (1950)	Grey	Translucent light yellow to dark yellow-brown particles	Yellow ochre
Red (1950)	Yellow	Fine birefringent particles of variable size	Red ochre
White (1950)	Bluish white	Fine and fairly uniform in size birefringent particles with interference colours.	Calcium carbonate white

Video microscope analysis

The video microscope acquisitions, performed on all the mosaic surface, consented also to plan the choice of the points for XRF measurements. The video microscope acquisitions were very useful for the characterisation of the *tesserae* in the angel eyes and mouth. These latter ones have the

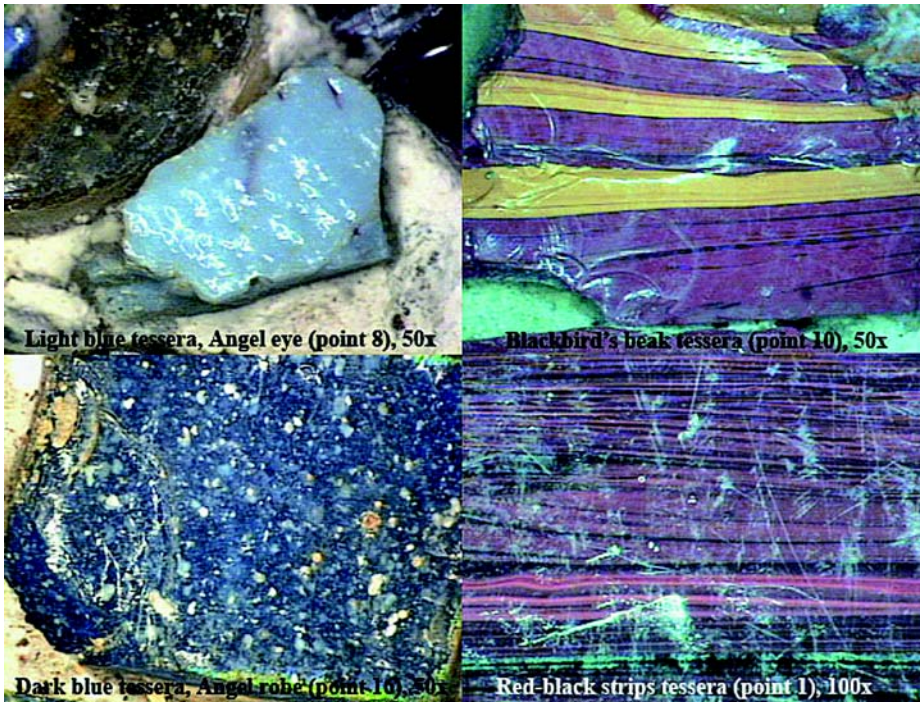

Fig. 4 – Video microscope acquisitions of different *tesserae*. Here are visible devitrification of the dark blue *tesserae* (point 16) and surface abrasions of the red-black strips *tesserae* (point 1).

peculiar hue of orange called *becco di merlo* (blackbird's beak) by Venetian mosaicists and glassmakers. Moreover, the acquisitions concerning the *tesserae* in the Angel eyes, mouth and robe evidenced typical deteriorations like devitrification and surface abrasions (Fig. 4).

XRF analysis

The XRF analysis was carried out on 35 *tesserae* and it allowed the determination of the chemical elements with atomic number higher than 19 (K) (Moioli et al., 2009). So the following materials were characterized by means of XRF measurements: impurities of the materials used in glass pastes production (barium and iron compounds often associated with strontium and rarely titanium and zirconium); opacifiers (antimony, calcium, lead, tin, zinc); metal oxides used for colouring the glass pastes (copper, cobalt, manganese, iron, etc.); other compounds added to modify the colour and the characteristics of the glass (antimony and manganese). In the most examined *tesserae*, the opacifiers were constituted by lead and tin compounds

(Table 2). Only two white investigated *tesserae* (points 09 and 49) were opacified by means of antimony compounds (Moioli et al., 1995). In several examined points antimony and tin were simultaneously determined, but the counts are so low that their addition seems to be not intentional. Also the green *tesserae* were opacified with antimony, in addition to the white *tesserae*, but the counts of this element are much lower than that of the white tesserae opacified with antimony compounds. The comparison between the counts of lead and tin in almost all the examined *tesserae* showed a certain correlation, so we can say that probably the glass pastes were coloured and opacified with lead and tin oxides in a constant weight ratio (calcined lead and tin, Fig. 5).

Tin and antimony were not present only in the grey *tessera* (point 19). Probably this is a colourless lead glass and the glass was opacified by means of micro air bubbles or silica (or other minerals) addition to the melted paste during the cooling process. This second hypothesis seems to be supported by the investigation through the video microscope.

Copper was present as colouring agent in some of the green *tesserae* and in the red-orange ones. This element was present also in the gold *tessera*, without *cartellina* (transparent glass cover), that got a red glass paste, in the black *tessera* (point 7) and in the red-black strips *tessera* (point 1). The copper traces, identified also in the blue *tesserae,* were probably due to impurities in the cobalt ores. Manganese was present in all the examined *tesserae*. Higher counts, compared to the iron ones, were determined in the violet *tesserae* (as colouring agent) and in the grey and gold ones (as decolouring

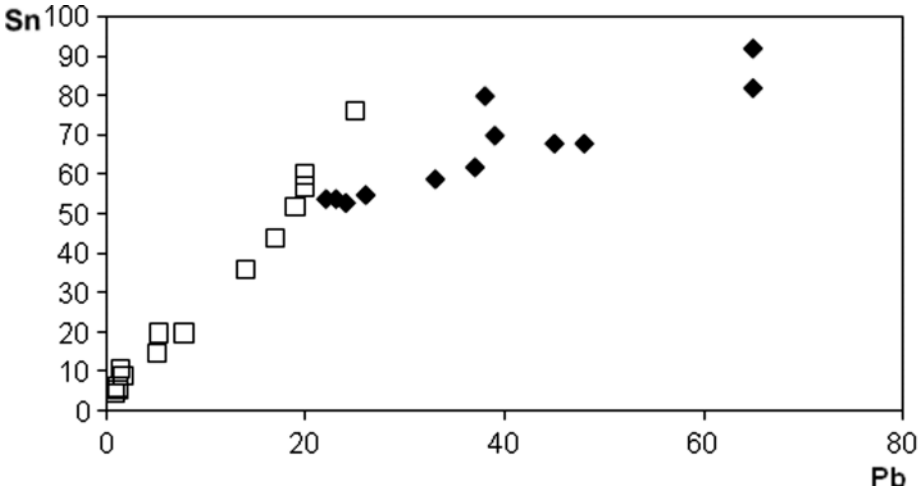

Fig. 5 – Fluorescence intensities of lead and tin (cps). Squares: blue, red, green, black and violet *tesserae*. Diamonds: other colours.

Tab. 2 – Fluorescence intensities for the detected elements (cps).

Pn	*Colour*	*Ca*	*Mn*	*Fe*	*Co*	*Cu*	*Zn*	*Au*	*Pb*	*Sn*	*Sb*	*Ba*
25	Blue	2.5	2.3	7.7	.59	tr	11		24	53		1.0
47	Blue	2.6	6.0	10	.81	tr	13		20	57		4.6
48	sky-blue	1.7	2.4	5.5	.78	tr	7.8		45	68		.96
26	dark blue	1.0	2.8	6.1	1.3	tr	7.5		23	54		1.9
17	light blue	1.5	1.1	4.4	tr	tr	5.0		33	59		tr
18	medium blue	3.4	1.4	6.2	tr	tr	3.8		22	54	.24	.95
16	dark blue	1.7	1.6	5.5	tr	tr	4.7		20	60		.99
08	light blue	1.3	1.3	3.1		2.5	1.8		65	82		.92
50	light blue	10	.65	6.1					7.8	20		1.0
20	bluish white	1.3	.57	1.5					48	68		.21
09	White	2.8	3.1	4.4						4.1	212	1.7
49	White	3.1	1.0	6.2					1.9		220	1.2
45	White	5.6		38					37	62		.82
19	Grey	3.8	7.4	6.0					70			1.6
07	Black	2.6	6.9	26		18			1.7	9.2	4.4	5.4
27	Red	2.1	3.0	38		47			5.3	20	.48	3.6
01	red-black	2.0	5.6	24		16			1.4	11	3.0	4.4
10	Orange	.94	.99	7.4		65			29	5.8	7.6	.67
03	Green	4.2	2.4	36					19	52		2.1
04	light green	1.4	2.0	29					38	80		1.1
21	light green	2.7	2.3	16					65	92		.36
22	medium green	2.7	5.1	51					39	70		1.1
02	dark green	3.6	5.0	63					17	44		2.0
06	semitransparent green	3.7	2.0	12					5.1	15		1.6
14	light emerald green	.82	3.2	4.4		15			10	2.5	11	2.9
15	dark emerald green	.85	tr	12		24			10	4.4	20	.88
13	green-yellow	1.2	7.2	14		6.3			17	3.1	11	2.1
24	light violet	1.2	2.4	2.9					25	76		1.0
05	medium violet	1.1	2.9	2.5					26	55		.72
23	dark violet	1.4	3.1	2.7					14	36		1.2
28	Gold	2.8	6.0	30		13		7.3	1.2	5.6	1.6	7.5
29	Gold	3.9	7.2	9.2				11	.95	4.9	1.9	10
46	Gold	4.0	8.6	10				6.4	1.2	6.4	1.2	9.1
11	pink (stony *tessera*)	28		.60								
12	dark pink (stony *tessera*)	23		.70								

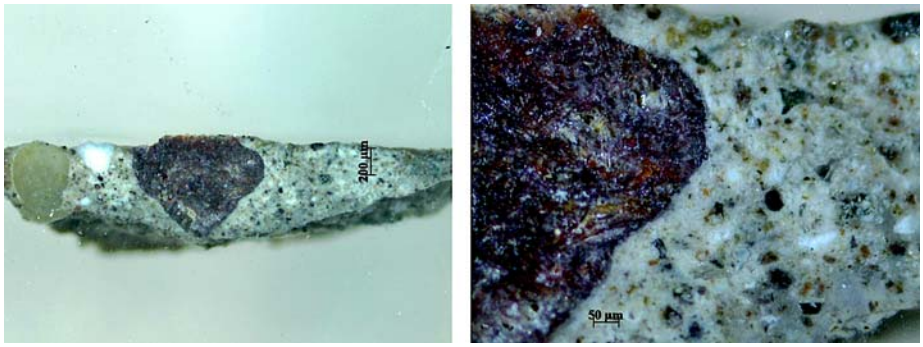

Fig. 6 – Cross sections at two different magnifications of the hard cementious mortar.

agent). In general iron counts were low. Only in some of the examined *tesserae* iron counts are more consistent and they seem to indicate a deliberate addition to obtain the colour, in particular in the green *tesserae* without copper (points 2, 3, 4, 22), in the gold *tessera* without *cartellina* (point 28), in the red *tessera* (point 27), in the black *tessera* (point 7), in the red-black strips *tessera* (point 1) and in the white *tessera* opacified with tin oxide (point 45). The colour of the blue *tesserae* was obtained with cobalt compounds systematically associated with zinc impurities.

FTIR and μFTIR analysis

The analyses of pigments and binders used for the false mosaic reintegration and for the modern paintings were carried out by means of polarizing microscope and FTIR spectrometry. The false mosaic reintegration was painted with a tempera based on a proteinaceous binder, probably aged egg (bands at 1717-1730cm^{-1}, 1630-1660cm^{-1}, 1536 cm^{-1}, 1237cm^{-1}, 1155cm^{-1} and 1110 cm^{-1}) (Meilunas et al., 1990; Derrick et al, 1999; Gracia, 2001; Lotti, 2009). The more recent paintings on the mosaic surface were realized with synthetic pigments with a polysaccharide binder (bands at 2934, 1624, 1445, 1322, 1089 cm^{-1}). These data were very useful for the choice of the solvents employed by restorers.

In order to discover the possible original setting bed of the *tesserae*, visible in the Scala archive photographs, eight samples were taken for the stratigraphic analysis. The examined cross and thin sections show the presence of a mortar made up of calcite and red hydraulic aggregates and an underlying layer composed by a very hard cementitious mortar (Fig. 6). Unfortunately these results suggest that the original setting bed is not present because it was completely replaced with a new mortar during the restoration carried out in 1950.

Conclusions

The reduced dimension of the mosaic fragment allowed to investigate it in depth, through a wide and integrated number of techniques. Provided information supported the work of the restorers by means of the identification of materials and the recognition of the entity of the previous restorations and their diversification. Original materials have been also investigated in depth, allowing a better comprehension of techniques associated to mosaic and glass production during 13^{th}-14^{th} centuries and their deterioration.

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