



DOI: 10.5281/zenodo.3364817

SPECTROSCOPIC ANALYSIS OF PIGMENTS OF THE ANTONELLO GAGINI ANNUNCIATION'S SCULPTURAL MARBLE GROUP, CHURCH OF ST. THEODORE MARTYR (BAGALADI, REGGIO CALABRIA, ITALY): CASE STUDY

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Received: 22/07/2019

Accepted: 30/08/2019

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ABSTRACT

This study is focused on the compositional and structural analysis of ancient gilds of the Antonello Gagini Annunciation's sculptural group, made in the last 1504 and now preserved in the church of St. Theodore martyr in Bagaladi, Reggio Calabria, Italy.

For this purpose, a combination of spectroscopic techniques was employed. X-ray fluorescence (XRF) spectroscopy was used for the quantitative elemental analysis of the investigated samples. In order to identify their crystalline mineral components and to study their microstructure, Raman Scattering (RS) measurements were carried out.

The chemical composition of the investigated samples allowed to identify elements and compounds, closely related to the sample preparation and preservation, with the aim to improve the knowledge of the gilding on stone materials in the late Renaissance and in order to suggest to restorers the best interventions to minimize the conservation problems that could affect the durability of the precious artefact.

KEYWORDS: X-Ray Fluorescence; Raman Scattering; Gilds; Annunciation's sculptural group

1. INTRODUCTION

The analysis of ancient artefacts, based on their composition, represents an important aspect of the new archaeological research. In particular, the patina layer, representing an important aspect of the artefact surface, endures strong changes as a consequence of the conservation environment, impacts with other materials, absorbent contaminants promoted by thermal and chemical processes, etc. Its composition may be changed as a result of the interaction between its constituting metal alloy and the environmental agents or contaminants. Compositional data are a fundamental tool in the study of ancient extractive and fabrication technologies.

X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray spectroscopy (EDX) associated to the Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), Raman Scattering (RS), Surface Profilometry (SP), Mass Spectrometric Techniques (MST), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Thermal Ionization Mass Spectroscopy (TIMS), Laser Ablation-Mass Quadrupole Spectrometry (LAMQS), represent only some of the many analysis techniques useful for these investigations (Anssens *et al.*, 2017; Caridi *et al.*, 2016; Liritzis *et al.*, 2018; Al-Emam *et al.*, 2015; Mezzasalma *et al.*, 2009; Dussubieux *et al.*, 2008; Bratitsi *et al.*, 2019; Ganetsos *et al.* 2019).

In the present study X-Ray Fluorescence and Raman Scattering spectroscopy have been used for experimental measurements, in order to analyze the chemical composition, to identify the crystalline mineral components and to study the microstructure of ancient gilds of the Antonello Gagini annunciation's sculptural group, made in the last 1504 and now preserved in the church of St. Theodore martyr in Bagaladi, Reggio Calabria, Italy (Medhat *et al.*, 2018; Milianni M. *et al.*, 2010; Centeno *et al.*, 2008; El-Rifai *et al.*, 2013).

The cultural heritage is made with blocks of white Carrara marble, of different sizes and thicknesses, sculpted both in the round and in relief.

It represents one of the main renaissance artworks of Calabria, and, in general, of the southern Italy and an its photo, with the provenience area of the investigated samples put in evidence, is reported in Fig. 1.



Fig. 1. Photo of the Antonello Gagini Annunciation's sculptural group, church of St. Theodore martyr in Bagaladi, Reggio Calabria, Italy, with the sampling locations.

2. MATERIALS AND METHODS

2.1 X-Ray Fluorescence

The chemical composition of the analyzed ancient gilds was investigated by XRF spectrometry; in particular, by using SPECTRO xSort instrument, a portable and compact analyzer (Spectro xSort, 2019).

Before conducting measurements, a standardization, also called ICALization, that includes the energy channel recalibration, was necessary and it was performed automatically by the instrument (Spectro xSort, 2019). The excitation source was a tube of Rh at 50 kV. The current intensity was changed, according to the analysed element and its quantity, in the range from 21 μ A to 125 μ A. A high sensitive and high resolution Silicon drift detector (SSD) was used.

XRF analysis was conducted directly on samples (dust) to ascertain chemical identification of the samples and if precious metals were contained inside them. In order to prevent the occurrence of leakage radiation, a docking station, available from the manufacturer, was used in this study. An outer protective film transparent adhesive tape, always provided by manufacturer, was placed over the sensitive window in order to protect the tube - detector system from any contamination due to the window opening during measurements.

2.2 Raman Scattering

Raman measurements were performed by using a DXR-SmartRaman Spectrometer (Thermo Fisher Scientific). The experimental set-up was equipped with 180 degree sampling accessory (Thermo Fisher Scientific, 2019).

The spectra were acquired using a diode laser source with the excitation wavelength of 780 nm. All

Raman spectra were acquired over the wavenumber range of 3400 – 50 cm^{-1} with a resolution of 1.9285 cm^{-1} and irradiated with a laser power of 24 mW, coming out from a 50 μm spot.

In order to obtain high signal to noise ratio (S/R), the Raman spectrum of each sample was obtained after collecting 32 sample exposures, and the duration of each exposure during data collection was set equal to 15.0 s. Total acquisition time was 8 minutes for each spectrum. All Raman spectra were stored in .SPA format and the post processing

analysis was performed by using the Omnic for dispersive Raman 9.0 software.

3. RESULTS AND DISCUSSION

3.1 XRF analysis

Three measurements were performed for each investigated sample, to obtain the mean concentration value (MCV), expressed in %, of each detected chemical element. The analytical error corresponds to the statistical one, with a confidence level of 95 % (2σ).

Results are reported in Tab. 1.

Tab. 1. The mean concentration value (MCV), expressed in %, and the analytical error (2σ), of each detected chemical element for the four investigated samples.

Sample 1	MCV (%) $\pm 2\sigma$	Sample 2	MCV (%) $\pm 2\sigma$	Sample 3	MCV (%) $\pm 2\sigma$
Fe	37.0 \pm 1.9	Fe	5.33 \pm 0.27	Fe	5.79 \pm 0.30
Cu	11.6 \pm 0.6	Sn	6.59 \pm 0.33	Cu	0.59 \pm 0.03
Pb	41.3 \pm 2.1	Pb	87.7 \pm 4.4	Pb	85.6 \pm 4.3
W	6.29 \pm 0.31	Ag	0.23 \pm 0.01	Sn	4.93 \pm 0.25
V	0.17 \pm 0.01	Cr	0.07 \pm 0.01	Au	3.22 \pm 0.16
Cr	0.19 \pm 0.01			Cr	0.085 \pm 0.001
Ti	0.21 \pm 0.01			Ti	0.11 \pm 0.01
Zn	1.60 \pm 0.08			Ni	0.028 \pm 0.001
Mn	1.57 \pm 0.08			Pd	0.092 \pm 0.001

Regarding to the sample 1, Pb (41.3 \pm 2.1) %, Fe (37.0 \pm 1.9) %, Cu (11.6 \pm 0.6) % and W (6.29 \pm 0.31) % are the most abundant chemical elements. Other minor ones detected are Zn (1.60 \pm 0.08) % and Mn (1.57 \pm 0.08) %. Ti (0.21 \pm 0.01) %, Cr (0.19 \pm 0.01) % and V (0.17 \pm 0.01) % are present in traces.

For the sample 2, Pb (87.7 \pm 4.4) %, Sn (6.59 \pm 0.33) % and Fe (5.33 \pm 0.27) % are the major elements, while Ag (0.23 \pm 0.01) % and Cr (0.07 \pm 0.01) % are present in traces.

For the sample 3, Pb (85.6 \pm 4.3) % is the most abundant one. Other minor ones detected are Fe (5.79 \pm 0.30) %, Sn (4.93 \pm 0.25) % and Au (3.22 \pm 0.16) %, while Cu (0.59 \pm 0.03) %, Ti (0.11 \pm 0.01) %, Pd (0.092 \pm 0.001) %, Cr (0.085 \pm 0.001) % and Ni (0.028 \pm 0.001) % are traces.

Experimental results underline that some decorations with gold plates, used by the artist for the gilding of the investigated sites, there is now some trace only in the sample taken from the site 3.

3.2 RS analysis

Raman spectra were acquired for each sample, in order to identify materials and pigments present in the investigated dust (Gutman et al., 2016).

Fig. 2 reports the Raman spectrum of sample 1.

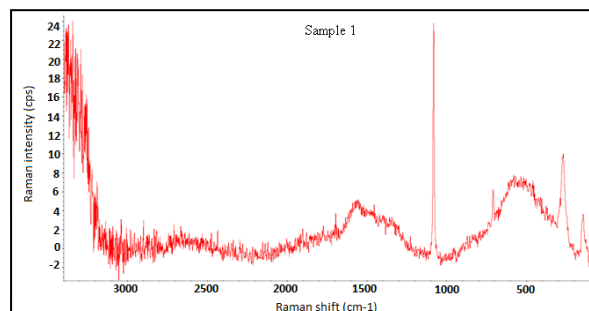


Fig. 2. The Raman spectrum of sample 1.

Peaks at 143, 706 and 1080 cm^{-1} are attributed to calcite, confirming the marble manufactured. Large bands centered at 530 and 1530 cm^{-1} are characteristic of Iron Gall ink (ferric gallate, $\text{C}_{21}\text{H}_{15}\text{FeO}_{15}$). The yellow color of the sample is attributed to the Massicot (lead oxide, PbO) at 288 cm^{-1} . Fig. 3 reports the Raman spectrum of sample 2.

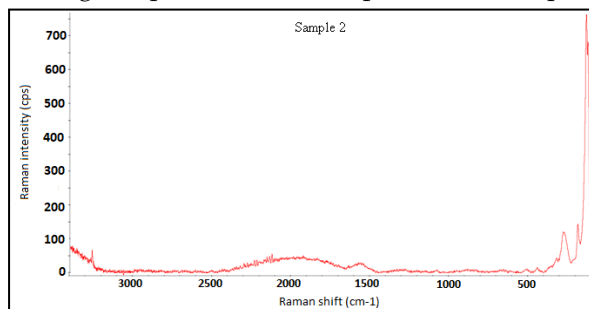


Fig. 3. The Raman spectrum of sample 2.

Calcite at 1080 and 1434 cm^{-1} , Lead stannate at 73, 122, 188, 273, 445, 512 cm^{-1} and Minium (lead oxide, Pb_3O_4), at 314 cm^{-1} were detected. The presence of Bistre Wood soot (carbon, C) band at 1560 cm^{-1} could be attributed to atmospheric pollutants.

From experimental results referred to samples 1 and 2 we can deduce that the gold plates, used in the hair of the announcing angel and in the moldings of the capitals, have been applied on a base of lead yellow, specifically lead oxide (Massicot, sample 1 and Minium, sample 2), a color with not very lively chromatic totality and excellent hiding power, identified in historical documents with the name of "giallorino", "giallolino" or "yellow of Naples" (Matteini et al, 1991), in use since the fifteenth century.

Raman spectrum of sample 3 is shown in Fig. 4.

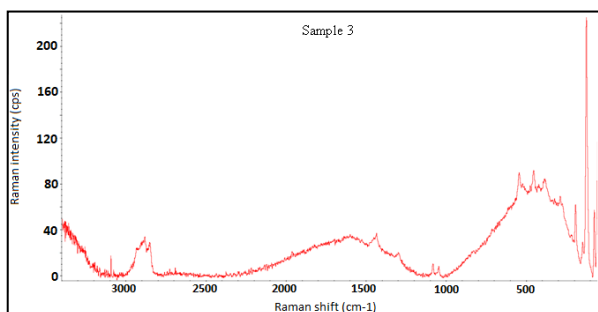


Fig. 4. The Raman spectrum of sample 3.

Also in this sample, peaks at 145, 270, 706, 1080, 1434 cm^{-1} are attributed to calcite. Those centered at 73, 122, 188, 386 and 455 cm^{-1} are characteristic of Lead tin yellow (lead stannate, Pb_2SnO_4). The Yellow ochre (Iron oxide hydrate, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ + clay + silica) is also present (at 547 cm^{-1}). Raman analysis confirmed the presence of Au. This element, detected by using XRF measurement, is present in the Raman spectrum bound with Cu (band centered at 2850 cm^{-1}), as deduced from a comparison with the study of (Lin et al., 2002). Haematite (iron oxide, Fe_2O_3) and White Lead Basic (lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) are also present.

These experimental results confirm that a different preparatory layer was employed on the veins of the acanthus leaves that decorate the column of the lectern placed between the Virgin and the Angel. On these reliefs, the yellow ochre was used, almost certainly as a substitute for the more common bolus, as was widely found in the gilding of stone artefacts from the fourteenth century (Andreuccetti, 2008; Cennini, 1995).

Raman peaks and bands for all investigated samples were identified by using the database

reported in (Marucci et al., 2018) and they are all summarized in Table 2.

Tab. 2. Identified Raman peaks and bands of all investigated samples.

Sample ID	Pigment name	Characteristic peaks (cm^{-1})
1	Massicot	288
	Iron Gall ink	530 (br), 1530 (br)
	Calcite	143, 706, 1080
2	Lead tin yellow (lead stannate)	73, 122, 188, 273, 445, 512
	Minium	314
	Bistre wood soot	1560 (br)
3	Calcite	1080, 1434
	Lead tin yellow (lead stannate)	73, 122, 188, 386, 455,
	Haematite	290, 1320 (br)
	Yellow ochre	547
	White Lead Basic	1048
	Calcite	145, 270, 706, 1080, 1434
	Au	1850 (br)

4. CONCLUSIONS

The aim of this work was to investigate the ancient gilds of the Antonello Gagini Annunciation's sculptural group, made in the last 1504 and now preserved in the church of St. Theodore martyr in Bagaladi, Reggio Calabria, Italy. To perform this study two different analysis were conducted: XRF and Raman measurements. The first one provides chemical identification, while Raman measurements give information about the characteristic vibration levels of each constituent.

Obtained experimental results suggest the use, by the artist, of techniques and materials for the mission gilding of stone artefacts, diffused only from the second half of the fifteenth century. This allows today to reinforce the thesis on the strong influence exercised by the Tuscan artistic culture in the plastic production of Southern Italy since the end of the fifteenth century, also allowing to recognize in the manufacturer of the sculptural group of Bagaladi the hand of an artist well updated to the artistic techniques in vogue in Renaissance Florence. A particularly significant indication, especially if related to the recent hypothesis on the formation of Antonello Gagini, probably not limited to the paternal workshop.

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