Microchemical Journal 140 (2018) 96–104

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Real-time MA-XRF imaging spectroscopy of the *Virgin with the Child* painted by Antonello de Saliba in 1497

Hellen Cristine dos Santos[a,d,*], Claudia Caliri[a], Lighea Pappalardo[a,b], Roberto Catalano[a], Andrea Orlando[a], Francesca Rizzo[a,c], Francesco Paolo Romano[a,b]

[a] INFN, Laboratori Nazionali del Sud, Via Santa Sofia 62, 95123 Catania, Italy
[b] CNR, Istituto per i Beni Archeologici e Monumentali, Via Biblioteca 4, 95124 Catania, Italy
[c] Dipartimento di Fisica e Astronomia, Università di Catania, Via Santa Sofia 64, 95123 Catania, Italy
[d] Instituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R, n.187, Cidade Unversitária, 05508-090 São Paulo, Brazil

ARTICLE INFO

Keywords:
Pigments
MA-XRF
Scanning
Historical paintings
Imaging spectroscopy

ABSTRACT

The 15th century painting marked a transition in the pictorial technique due to the introduction of oil painting. Antonello de Saliba is a remarkable Sicilian painter that helped to disseminate this technique in Southern Italy. In this work, we present and discuss the technical examination of the *Virgin with the Child,* a wood panel painted by de Saliba in 1497 and on view at the Castello Ursino Museum in Catania (Italy).

The painting was investigated *in situ* by the use of a novel MA-XRF fast scanner allowing a real-time imaging of the chemical elements characterizing the pigments in the painting. Results allowed us to better elucidate the palette of the artist and its painting technique. The presence of restorations has been evidenced as well and correlated to different interventions occurred over the time.

1. Introduction

Antonello de Saliba (1466–1535) was strongly linked to Antonello da Messina. Saliba was his nephew and having been his apprentice for different periods of his life. However, the artistic maturity of Antonello de Saliba was reached in the workshop of the Venetian painter Giovanni Bellini. Many of his artworks present an evident influence from the Venetian school and testify his activity in North Italy.

The *Virgin with the Child* is the first documented work of Antonello de Saliba after his return to Sicily, where he worked for about 40 years. The memories of his period in Venice are vivid in this artwork and give a delicious freshness to the colors and a special charm to the figure of the Virgin. The hypothesis that this could be the central part in an altarpiece panel pushed art historians to identify other three panels that are stylistically similar to the artwork even if they present a more modest quality [1].

In this work, we present the study of this historical painting by means of the mobile MA-XRF (Macro X-Ray Fluorescence) scanner developed at the LANDIS laboratory of Catania (Italy), in the framework of collaboration between the Italian National Research Council (IBAM-CNR) and the National Institute on Nuclear Physics (INFN-LNS).

It is no wonder that the MA-XRF has been extensively applied to characterize inorganic paint ingredients as pigments and fillers of historical paintings, in a nondestructive way, and has been reported with success in various works published in the scientific literature [2–9]. Since the first works on this issue, many improvements have been done [10,11]. Among the factors that contributed to the improvement of this technique, we can mention the development of data acquisition electronics and software development of remote control of the axes that sustain and are responsible for the movement of the measurement head. Making possible faster, *in situ* and multi-elemental real time analysis, where large areas of paintings can be covered in a few hours, resulting at the end of the measurement, elemental maps ready to be viewed by the user [12].

The procedure to obtain an elemental distribution map using MA-XRF imaging technique begins with the acquisition of a spectrum for each scanned point over all surface of the object under analysis (*e.g.* one spectrum per pixel). The acquired spectra will originate what we call of a hyperspectral data cube. The information about the position and it associated spectrum will be used to reconstruct the elemental distribution map. The next step is to process the hyperspectral data cube using a computer code. In an image obtained using conventional radiography, the contrast representing in grayscale is due to the different density presented by the compounds of the sample. Nothing about the elemental composition can be argued. In the case of MA-XRF imaging, the contrast is built according to the change in signal strength

* Corresponding author at: Instituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R, n.187, Cidade Unversitária, 05508-090 São Paulo, Brazil.
E-mail address: hsantos@if.usp.br (H.C. dos Santos).

https://doi.org/10.1016/j.microc.2018.04.015
Received 20 September 2017; Received in revised form 17 January 2018; Accepted 12 April 2018
Available online 19 April 2018
0026-265X/

and the abundance of the chemical elements. Thus, unlike the radiographic method, it is possible to reconstruct the different pigments used in the composition of a painting.

The data process consists in adjust each XRF spectrum of the hyperspectral data cube by the application of an analytical model, then recreate the image of the painting in terms of the elemental distribution [13,14]. Therefore, information concerning the nature of the inorganic pigments and fillers can be extracted by evaluating the elements identified on spectra and their distribution over the painting surface and subjacent layers.

The study of paintings of such period marked by several changes in the painting techniques is a very important issue and a challenge for MA-XRF imaging spectroscopy. Results obtained in this work led us to report insights about the creation process of the artist, the palette of pigments, and to investigate on the previous restorations and the actual conservation state of the artwork. This work contributes to fill the lack of information about Sicilian artists who gave great contributions to the techniques of paintings developed during the pre-Renaissance that were later spread by Renaissance artists.

2. Material and methods

2.1. The painting Virgin with the Child by Antonello de Saliba

The painting *Virgin with the Child* is shown in Fig. 1. It is an oil painting on a wood panel of 125 × 77 cm^2, being one of the most appreciated paintings in the gallery collection of the Castello Ursino Museum in Catania (Italy). Due to its high quality, it has been attributed for a long time to the old master Antonello da Messina. In fact, the original signature of Antonello de Saliba was lost in the panel due to a general degradation of the pictorial layer and to different retouches and repainting occurred over the time. The correct attribution of the artwork was obtained in 1920 when a restoration evidenced the date, the 2nd July 1497, and the signature of Antonello de Saliba. Further conservative known treatments have been performed in 1953 and 2003 [1].

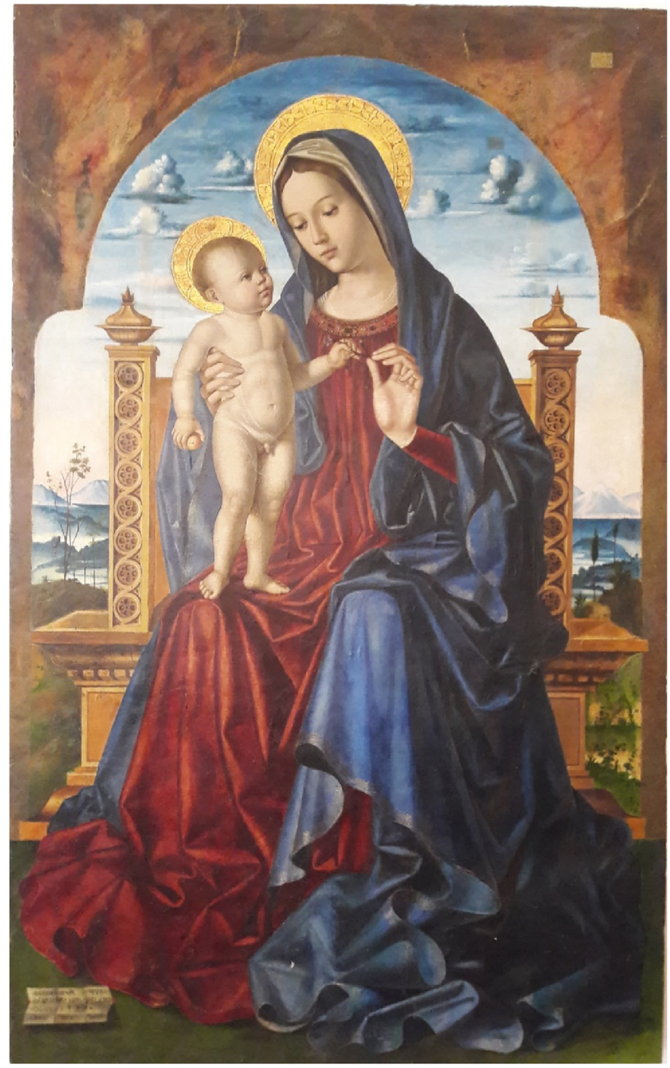

Fig. 1. *Virgin with the Child*, 1497. Oil on wood panel (125 × 77 cm), Castello Ursino Museum in Catania (Italy).

2.2. The real-time MA-XRF scanner

The identification of pigments in the painted panel was achieved by using the LANDIS-X device developed at LNS-INFN and IBAM-CNR in Catania (Italy). LANDIS-X is a mobile X-Ray scanner integrating MA-XRF, micro-XRF and confocal XRF analytical techniques for investigating large dimensions painted artworks. In this work only elemental distribution images have been obtained by using the MA-XRF technique, micro-XRF and confocal-XRF were not performed due to the limited time of access to the painting. LANDIS-X consists of a measurement head equipped with a Rh-target X-ray tube focused with a polycapillary lens presenting a 25 μm spot diameter at 1 cm focal distance and at the Rh-K energy (X-ray tube and polycapillary by IFG). At this focal distance, LANDIS-X is used as a high-resolution micro-XRF spectrometer. MA-XRF measurements are performed by positioning the samples at about 1.5 cm from the measurement head where the beam size is about 500 μm. X-ray spectra are collected during the scanning by means of two SDD detectors (by KETEK) with an energy resolution of 130 eV at 5.9 keV and 50 mm^2 active area. They are operated in parallel with two Digital X-ray Processor (By BRIGHTSPEC) working in a time-list-event-mode (TLIST) with 40 ns resolution. X-ray source and detector are in a 45-90-45 geometry. A detailed description of the detection procedure is given in reference [12]. The information of the setup is summarized in Table 1.

Table 1
Summary of the XRF scanner.

Parameter	Value
X-ray source	30 W Rh-anode tube
Focusing optic	Polycapillary with a focal distance of 1 cm
Beam size at the focus	25 μm diameter at the energy of the Rh K-lines
SDD detector	50 mm^2 active area; 133 eV energy resolution at 5.9 keV
Measurement geometry[a]	45°-90°-45° detecting-incidence-detecting angles
Area of scansion	110 × 70 cm^2 (maximum value)
Step-size[b]	1–50 μm in the scanning micro-XRF 50–500 μm in the scanning macro-XRF
X-ray source parameters	38 kV and 0.6 mA
Dwell time	20 ms (including overhead)
Measurement time	4.7 h for a 400 × 1400 pixels image corresponding to 56 × 10^4 local XRF spectra measured in the sample surface (Macro-XRF)

[a] With respect to the sample surface.
[b] Depending on applications and sample dimensions.

Two custom-designed long-range linear axes allow covering an area of 110 × 70 cm^2. The absolute position of the X-ray beam on the painting during scanning is obtained with a wire sensor allowing sub-micron accuracy. No referencing or calibration of the axes is needed before starting the measurements and position is maintained even when the system is switched off/on (*i.e.* during closing time of the Museum). Alignment of the beam at the measurement position is achieved with a long distance microscope supported by a laser sensor for measuring the distance between the spectrometric head and the sample under