# IRR and XRF investigations on Annunciata by Antonello da Messina to trace the original appearance of The Blue Veil

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Over a century of restorations, archival documents, research, diagnostic investigations and exhibitions around the world to tell an icon of beauty in Sicily.

Fig. 1 - Antonello da Messina, Annunciata: a) Rome, ICR, 1942, the painting during the restoration directed by C. Brandi; the extensive repainting are visible as well as the five areas with raising the colours; b) Annunciata after the restoration (images owned by the Istituto Superiore per la Conservazione e il Restauro, Rome, Italy, ©Photo Archive).

## INTRODUCTION AND RESEARCH AIM

The study of paintings, because of their compositional complexity, often requires the combined use of integrated spectroscopic methodologies and diagnostic imaging techniques. In this way, it is possible to exploit the correlation between data on a small spot analysis to those of larger scale.

For more than 30 years, among the possible qualitative and quantitative spectroscopic analyses, X-ray fluorescence (XRF) proved to be one of the most informative methods. Current scientific studies are aimed at improving key features to maximize the value that this technique can provide in this Archaeometry field. Recently, the efforts of the Cultural Heritage scientific community have been addressing the development of new combined systems to increase the chemical detection capability (Trentelman et al. 2010; Hocquet, et al. 2011; Alfeld et al. 2011; Romano et al. 2017). The goal has always been twofold: on one hand, to achieve higher resolution and analyse, in a non-invasive way, each layer along a stratigraphic structure; on the other hand, to attain 2D elemental mapping, on extended painted surfaces in shorter time. Indeed, in many cases, it is not a single point test which is of interest, but the distribution of elements across a defined pictorial surface. This target can be met by acquiring XRF line and area scans. The latest improvements on XRF systems see the devices combining different analytical methods and non-invasive imaging techniques. For *in situ* diagnostic studies, the use of elemental mapping can help identify an artist's characteristic palette and painting technique revealed by Infrared Reflectography (IRR). Also, it helps to reconstruct the conservation history related to undocumented previous restorations.

Starting from these new technological possibilities, a deeper diagnostic investigation on the *Annunciata* painting by Antonello da Messina (Antonio di Giovanni de Antonio; Messina, 1430-1479) was carried out by using INTRAVEDO scanner for IRR and XRF mapping, in order to investigate, thanks to an innovative equipment, some technical features of this work of art up to date remain unclear.

The *Annunciata* (oil on poplar wood, 45×34.5×0.5 cm), painted around 1476, is currently displayed at *Galleria Regionale di Palazzo Abatellis* in Palermo (Sicily) in the *Sala di Antonello*. As reported by Antonino Salinas and Vito Fazio Allmayer in 1907 (Salinas 1907; Fazio Allmayer 1907), the painting became part of the museum collection, the then National Museum of Palermo, in 1906. It was a donation by Mrs. Francesca Tamburello da Salaparuta, sister of Monsignor Vincenzo Di Giovanni, last owner of the painting, who ordered the donation after his death.

Salinas also reported (Salinas 1907) that, at the beginning, Monsignor Gioacchino Di Marzo discovered the panel, which was already worm-eaten, in the house of Barone Colluzio of Palermo, the first owner. Di Marzo then revealed the importance of the

painting to Monsignor Di Giovanni, who subsequently became the owner of the painting.
Fazio Allmayer reported (Fazio Allmayer 1907) that at first Di Marzo attributed the painting to Antonello De Saliba (Di Marzo 1899), and only at a second time he changed his opinion by recognising its paternity to Antonello da Messina (Di Marzo 1903). Brunelli, in 1906, attributed irrefutably this painting to Antonello da Messina (Brunelli 1906; Devitini & Righi 2007). Fazio Allmayer reported that the *Annunciata* at *Gallerie dell'Accademia* in Venice was a copy and not painted by Antonello de Saliba, as commonly recognised, but by Pietro de Saliba passing himself as Antonello in his best-made paintings, while for those of lesser quality he signed as Pietro de Saliba (Fazio Allmayer 1907). Di Giovanni had the painting restored by Louis Aloysio Pizzillo (in an unspecified period of the second half of 19th century). Pizzillo, who was at that time a well-known restorer in Palermo, carried out a heavy cleaning, according to restoration concept in that period, repainting of missing parts, colour retouching and mergering the old with the new through the layers of paint. Also, Enrico Brunelli, in 1906 about the donation of the painting to the museum, reported that this had been poorly restored (Brunelli 1906; Fazzio 2007). Indeed, the retouching had altered the hands, in particular the right hand, followed by a "drastic shaving", as well as the face of the Virgin, by scraping even the left eyebrow, while all other repaintings had been made on the dirty surface. The aging of protective varnish and consequent chromatic alterations of the paint changed the appearance of the veil, especially on the left side of the Virgin, blurring the fold over the hand (on the left side) (Brunelli 1906; Brandi 1942). Since the *Annunciata* became part of the collection of the National Museum of Palermo in 1906, probably the painting did not go through other restorations. Even if Filippo Ciaccio, restorer of the museum, remembered that between 1912 and '13 the former inspector Matranga deemed it appropriate to restore the painting. Because in the museum archive there was no trace of such action, the restoration was likely not done (Archivio Restauri ISCR, 14th March 1942).
On the occasion of the *Mostra dei dipinti di Antonello da Messina* in 1942, curated by Cesare Brandi, former director of the *Istituto Centrale per il Restauro* (ICR) of Rome, the painting was sent to the Institute. It was restored again as reported by the same Brandi. Meanwhile its condition had slowly altered due to: five colour layers raised in the direction of the wood grain; blackened widespread restoration (Archivio Restauri ISCR, 13th March 1942); inequality of products used for the previous cleaning, mainly carried out on the flesh tones (Fig. 1).
The panel, slightly curved, showed some fractures on the back and many holes of woodworm though still protected by the old primer. The X-ray radiographies revealed the closure of the worm holes by repainting over (Brandi 1942).
The restoration was performed, under the scientific direction of Brandi, by the restorer Luciano Arrigo. After the investigation of the entire surface under ultraviolet lamps and X-rays, the restoration was consisted of: consolidation of unsafe parts of painting; removing the paint due to old restorations; rebalancing the cleaning, and an armature sliding on the back of the wood panel. The cleaning of the painting in 1942 revealed: the fold of the veil over her right hand; the reflections under the lectern; the flashes of light when the page is cut, all of which appeared in the contemporary copy of the *Gallerie dell'Accademia* in Venice. Moreover, the faint perspective of the elliptical golden nimbus was removed, thanks to the radiographic survey in comparison to its copy in Venice, considered as realised at a later period, as well as the inscription (Brandi 1942; Archivio Restauri ISCR 13th March 1942).

**Fig. 2 - Palazzo Abatellis, Sala di Antonello, in situ investigations using INTRAVEDO equipment, an ultra-high-resolution IR and XRF scanner.**

After the ICR restoration in 1942, there were no other documented restorations except minimal interventions carried out by Franco Fazzio in 2005 followed by national and international temporary exhibitions. However, some elements suggested other interventions, such as the removal of the patina on the left side of the veil, compared to the photographic images of ICR when the restoration was completed (Fig. 1b), there were no shadows (Fazzio 2007).
During the last century, the painting was transferred for several temporary exhibitions, not only in 1942 (for the cited exhibition in Rome), but also in 1935 (Paris), 1953 and 1981 (Messina) (Bottari 1953; Regione Siciliana 1981).
More recently, in this century from 2005 to 2007, the *Annunciata*, was involved in non-invasive investigations (Ultraviolet Fluorescence acquisition, Infrared Reflectography and Infrared False Colour CCD imaging, X-Rays radiographic and tomographic investigations) (Cacciatore et al 2007; Salerno et al. 2007, Prestileo & Bruno 2007; Prestileo et al. 2009; Salerno 2010).
The main purpose of these investigations was to evidence the state of conservation considering the movement of this precious masterpiece during some temporary national and international exhibitions of Antonello da Messina: New York – Metropolitan Museum (2005-2006); Rome – *Scuderie del Quirinale* (2006); Taormina, Museum of *Palazzo Corvaja* (2007); Cefalù – *Fondazione Mandralisca* (2007); Milan – *Museo Diocesano* (2007) (Barbera 2005; Lucco 2006; Biscottini 2007; Lucco 2009).
Nowadays, the painting is part of the exhibition *Antonello da Messina* held at *Palazzo Abatellis* (Palermo), at its historical location (December 2018 - February 2019) and at *Palazzo Reale* of Milan (February-June 2019).
The preliminary studies, before *Annunciata*'s departure for the exhibitions in 2006, improved the knowledge on execution technique, materials used and past restoration interventions. This masterpiece was also included in the diagnostic campaign carried out by G. Poldi and G.C.F. Villa and published in the catalogue for the *Scuderie del Quirinale* exhibition in 2006. These non-invasive investigations techniques were performed in 2006 on 30 works of art, aimed at the study of the palette and the executive technique, constituting the first systematic scientific study of Antonello's *corpus*. The results showed that, although Antonello did not use a wide range of palette, he was able to take ad-


**Fig. 3 - Antonello da Messina, Annunciata: a) IR Reflectography (2015); b) details of the face and the veil; c) detail in IR False Colour (2006).**

vantage of the materials available, typical during the 15th century palette. This gave volumes, tones and *chiaroscuro* through mixtures and glazes, calibrating thickness and typology of the stroke; increasing thick-looking texture of the surface fabric, or very thin layers for the flesh tones and the highlights. These surveys also showed a variety types of underdrawings found in the many work of arts (Poldi & Villa 2006a; Poldi & Villa 2006b; Villa 2006; Benizzoni et al. 2007; Poldi 2009).

Subsequently, a decade on, the new diagnostic study in this paper, was carried out in 2015 directly *in situ*, in the *Sala di Antonello* of *Palazzo Abatellis*, by using XRF-IRR INTRAVEDO scanner. The study provided new elements specifically for a correct interpretation of the variations and alterations of shadows and lights in the veil over the time and of the painting area between the face of the Virgin and the blue veil. This pictorial surface, altered in the past by cleaning interventions, was not studied in depth during the previous scientific investigations as documented in 2007 by Franco Fazzio in his technical condition report (Fazzio 2007). In the case of the paintings analyses, the combined equipment for performing IR Reflectography and XRF investigation becomes particularly interesting because the X-ray fluorescence results complete the information from the diagnostic IR imaging. In fact, IRR highlights aspects no longer noticeable in the visible range or hidden by superficial layers, and the XRF mapping contextually returned the elemental composition of the overlapped pictorial layers, supporting the understanding of the pictorial stratigraphy and the distinguishing of any integration areas.

## MATERIALS AND METHODS

The previous and the new investigations of the *Annunciata* has always been carried out *in situ*, in the *Sala di Antonello* at the *Galleria della Sicilia di Palazzo Abatellis*, with portable instrumentation, by keeping the panel in its showcase in the closing day of the museum (Fig. 2).

The previous False Colour Infrared investigations (Cacciatore et al. 2007; Prestileo & Bruno 2007; Prestileo et al. 2009) were performed by using a Digital CCD Artist camera (with 23 mm F/1.4 lens and objective from 18-108 mm F/2.5) by Art Innovation. The images acquisitions were made using the CPS100 manual positioning system, as sources of lighting, of two 50W halogen lamps (for shooting in the visible and infrared up to 1150 nm).

The new investigation was carried out by using INTRAVEDO scanner, an ultra-high-resolution IR and XRF scanner (and positioning system Scanner XY: useful size 1.8×1.8 m, SW for positioning with 0.1 mm step reproducibility), to acquire *in situ* XRF mapping, for analysing the chemical composition of the pictorial layers characterized by different spectral response in the IR range.

Indeed, in order to utilise an XRF mapping acquisition system, a XY scanner was optimized and integrated, from both a software and hardware point of view.

The equipment is composed by a motorized XY scanner, constituted with a modular and light structure, to provide IR digital Reflectography through an InGaAs sensor. Starting from this instrumental apparatus, the scanner was integrated with an automatic positioner system, capable of supporting a maximum weight of 5 kg. This allows the housing of other equipment for not-destructive imaging and spectroscopic investigations. Among the various opportunities, a system for X-Ray fluorescence analysis coupled with the automatic positioner scanner provide several advantages. They guarantee a set-up of constant measurement and controlled geometry, aimed at creating False Colour maps for the determination of the spatial and stratigraphic distribution of the individual chemical elements revealed.

The XRF portable instrument consists of a miniature X-ray tube system. This includes the X-ray tube (max voltage of 40 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics and the USB communication for remote control; a Silicon Drift Detector (SDD) with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line Energy Resolution (depends on peaking time and temperature); 1 keV to 40 keV Detection range of energy; max rate of counts to $5.6 \times 10^5$ cps; software for acquiring and processing the XRF spectra. Primary beam and detector axis form an angle of 0 and 40 degrees respectively directly pointing towards the sample surface. Measurement parameters were as follows: tube voltage 35 kV; current 80 μA, acquisition time 60 sec for single shot and 20 sec for each spectrum acquired for lines scanning; no filter was applied between the X-Ray tube and the sample; the distance between sample and detector was 1 cm. The setup parameters were selected to ensure a good spectral signal and to optimise the signal to noise ratio (SNR).

## RESULTS AND DISCUSSION

The Infrared Reflectography obtained by the InGaAs sensor at 1700 nm confirmed the executive details shown by previous IR acquisition (Poldi & Villa 2006a; Poldi & Villa 2006b; Cacciatore et al 2007; Prestileo & Bruno 2007; Prestileo et al. 2009), highlighting higher resolution to reveal several changes made by Antonello and the pictorial areas to previous restoration treatments. In particular, the size of the thumb of the right hand has been changed by the artist three times, the little finger of the same hand was more bent compared to the first draft. Besides, the middle finger of the left hand was slightly inclined compared to the first draft in which it appeared relaxed and, therefore, longer. Moreover, in the Virgin's face, the underdrawing traces revealed the areas of shade (area to the left of the nose and under the chin) and details of the hair. The flicker holes of the xylophagous insects, stuccoes and pictorial integrations due to 1942 restoration (Brandi 1942; Archivio Restauri ISCR 13th March 1942; Archivio Restauri ISCR 14th March 1942) have been highlighted (Fig. 3). Previous investigations in Infrared False Colour already suggested a spectral difference between the inner portion of the veil along the left cheek of the Virgin (Fig. 3) characterized by a different tone than the entire veil that reveals the typical red spectral response of lapis lazuli blue pigment. This is not distinguishable in visible image (Cacciatore et al. 2007; Prestileo & Bruno 2007; Prestileo et al. 2009).

The different spectral response in the area between the face and the veil confirms the need to understand if this surface is affected by the thinning of the original blue layer, or instead, due to a possible undocumented pictorial integration real-

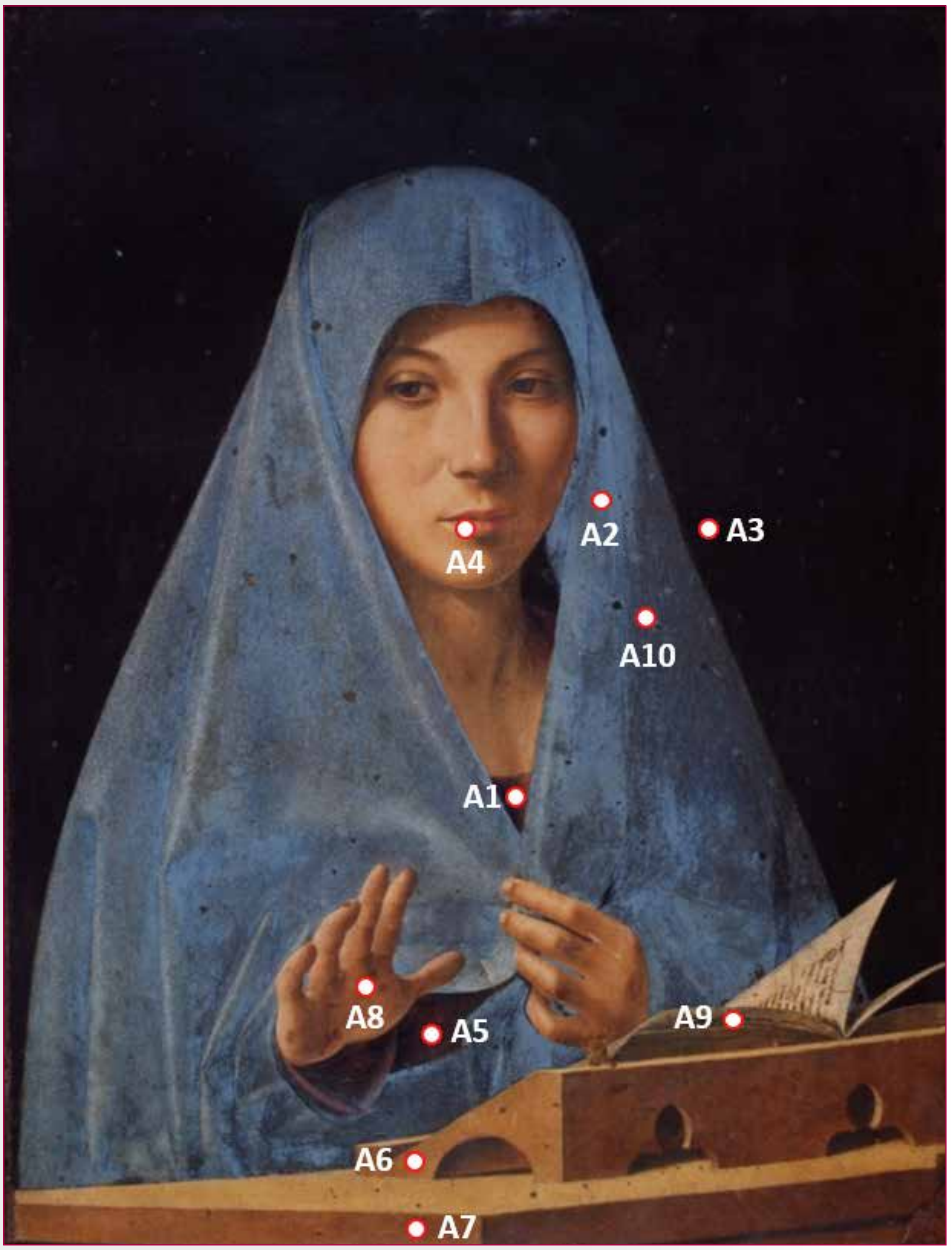


Fig. 4 - Antonello da Messina, Annunciata: localization on photographic image of XRF single spot measurements carried out to identify the pigments used on the different layers of colour and selected marker element for the XRF mapping analysis.

| ID area | Colour | Si Ka | S Ka | K Ka | Sn La | Ca Ka | Fe Ka | Cu Ka | Hg La | Pb La | Sr Ka |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | Dark Red | ND | 1847 | 1150 | ND | 3147 | 4698 | 1577 | 1200 | 30544 | 527 |
| A2 | Light Blu | 460 | 1519 | 1761 | ND | 3953 | 1575 | 619 | ND | 11823 | 1201 |
| A3 | Black | ND | 1575 | 950 | ND | 19581 | 813 | 8485 | ND | 851 | 1505 |
| A4 | Red | ND | ND | 378 | ND | 1073 | 1491 | 510 | 1265 | 32605 | 629 |
| A5 | Dark Red | ND | 2060 | 1793 | ND | 18125 | 980 | 772 | ND | 1019 | 1890 |
| A6 | Brown | ND | ND | 880 | 1455 | 6717 | 4282 | 439 | ND | 16004 | 1429 |
| A7 | Brown | ND | ND | 773 | 1444 | 2351 | 1075 | 556 | ND | 32789 | 718 |
| A8 | Flesh tone | ND | ND | 539 | ND | 3687 | 7712 | 510 | 895 | 19391 | 1360 |
| A9 | White | ND | ND | 344 | ND | 1366 | 1098 | 406 | ND | 30811 | ND |
| A10 | Dark blue | 270 | 1331 | 1394 | ND | 3931 | 1166 | 523 | ND | 13067 | 879 |

Tab. 1 - Chemical elements detected by XRF single spot measurements. The intensity values, expressed in total counts, refer to Kα or Lα peaks of each element; "ND" (Not Detected) refers to the absence or the presence below the detection limits for that element.

ized after the ICR restoration of 1942. Moreover, the darker grey-red colour of some veil area highlights the pictorial surface involved in typical lapis lazuli degradation named ultramarine disease, generally favoured in presence of oil as the binder (de la Rie 2017).
This pigment degradation and the loss of the glazes that traced back to the *chiaroscuro*, caused the failure of the volumetric rendering, key aspect of Antonello's technique.
Therefore, to contribute to the understanding of the alterations compromised by the blue layers, a deeper XRF was carried out in particular on the area between the face (already affected by historical additions) and the veil in the surface where the degree of shadows and volumes was altered. Preliminarily, the new diagnostic campaign involved the XRF analysis on 10 selected areas (Fig. 4) for the useful single-spot acquisition to systematically identify the original pictorial palette, only partially described in the literatures (Poldi & Villa 2006a; Poldi & Villa 2006b; Villa 2006; Benizzoni et al. 2007; Poldi 2009; Bellucci et al. 2010; Grassi 2009; Russo & Alvino 2012). In this way, it was possible to investigate the chemical marker of each original layer and consequently to provide valuable information to design the XRF mapping on the surface. This area was characterized by different FC Infrared spectral responses and by altering the shades, with respect to past photographic documentation (before than 1953).
Table 1 shows the identified chemical elements for each of the 10 areas under investigation. The results suggest the use of lead white (pure for white layer or mixed in all analysed pictorial layers), cinnabar (used in very low content and mixed with iron-based pigment, ochres or earths, for flesh tone and light red layers), copper-based pigment (constituting the dark background, also below the Virgin figure as confirmed by the low counts constantly detected in all XRF spectra), tin-lead yellow (used to make both light and dark wood colour) and lapis lazuli (pure, for the blue veil). Not noticeable XRF differences have been revealed between A2 and A10 measurement areas. Moreover, the use of lake or dye is suggested on the red layers of the dress of the Virgin.
The XRF scanner, compared to the acquisition of a single spot, can provide important information on the succession stratigraphic structure of the pictorial layers. It returns a mapping of the intensities of signal for each identified element, directly showing the existing correlation between the identified chemical elements. In fact, the elemental maps also represent a statistically significant collection of spectra, whose peak characteristic can be further analysed. This helps understand the different attenuation phenomena from the X radiation (evaluation between the relative intensities of the characteristic peaks), as well as the relative position of the layers and their thicknesses.
Starting from the preliminary XRF data on the elemental composition of flesh tone (face and hands), light blue (veil) and dark green (background), a linear mapping was provided on the area of interest to understand the alteration and stratigraphy of the pictorial blue layer (Fig. 5). The scanning analyses involved the mercury, lead, iron, copper, silicon and potassium intensity values to map the elemental composition variation. In particular, Hg and Fe are markers of face layer; Cu is the marker of background (underlying layer); Si and K as markers of blue veil layer (including inner area).

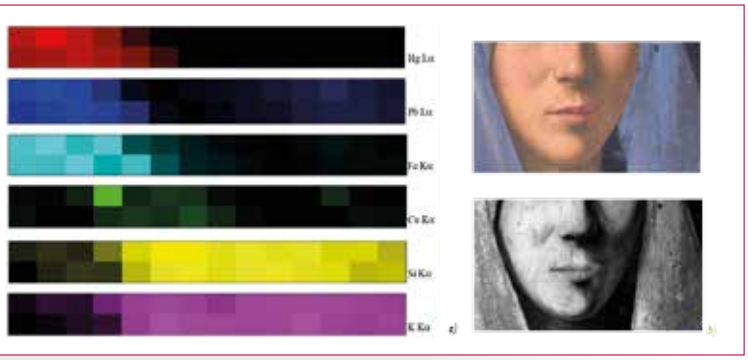

Fig. 5 - Antonello da Messina, Annunciata: a) mercury, lead, iron, copper, silicon and potassium line maps. The iron is totally absent in the area of the veil that in the past was affected by a dark layer of ochre or earth to define the shadow.

Indeed, the XRF mapping investigations revealed that the blue traces, characterised by the different spectral response in FCIR, in this area are not pictorial integrations added to the background layer during the past restorations. Rather, they are residuals of the original lapis lazuli layer constituting a portion of the blue veil which has been thinned during the 19th century intervention. Moreover, in the area of the veil where the alteration of the original shadows was found, the absence of iron confirms the removing or the thinning of a superficial veiled layer, typical of the Antonello's technique, generally performed with iron-based pigments (ochres, earths). This was no longer present and maybe totally removed during an undocumented intervention between the 1953 and 1981, as assumed by comparing the archival photos with the more recent ones of this painting since the 1980s (Vigni 1952; Regione Siciliana 1981).

## CONCLUSIONS

The present study provided a review of the conservative history, from the 19th century to the present, of the *Annunciata* by Antonello da Messina. It examined the archival documentation related to the documented restorations between the end of the 19th century and the 20th century. It includes the temporary exhibitions to which the *Annunciata* was part of, the previous diagnostic campaigns for the study of the executive techniques and the state of conservation on both the wooden support (original and of restoration) and on the pictorial layers.
The new diagnostic study was carried out by using INTRAVEDO scanner for IR Reflectography (InGaAs detector) and XRF mapping in order to investigate the painting area between the face of the Virgin and the blue veil and to identify the whole pigment palette in this painting. The new findings presented for the first time in this paper, together with a critical reading of the archival sources, have provided an important explanation of a correct historical-artistic reading of the original appearance of the subject. This study also represents a scientific support to clarify the conservation history which leads the painting to its current feature.

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## Abstract

*A new diagnostic investigation on Annunciata painting by Antonello da Messina was carried out in situ, in the Sala di Antonello of the Galleria Regionale di Palazzo Abatellis in Palermo (Sicily). It was carried out by using INTRAVEDO scanner for IR Reflectography (InGaAs detector) and XRF mapping, in order to investigate, thanks to an innovative equipment, the blue painting area, and in particular, the area between the face of the Virgin and the blue veil (on her left side). This pictorial surface, probably altered in the past by a heavy cleaning (date back to the 19th century) that involved the face and hands, was not clearly understood during the previous scientific studies. The finding here has provided an important assumption for a correct historical - artistic reading of the original appearance of the subject and represent a scientific support to clarify the conservation history which leads the painting to its current state. The new studies provided a common understanding of the available archive information, previous restorations and diagnostic investigations carried out over time.*



## Parole chiave

**Antonello da Messina palette; lapis lazuli; MA- XRF; IR False Colour; IR Reflectography**



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