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Authors: Jana Striova, Chiara Ruberto, Marco Barucci, Jan Blažek, Diane Kuzman, Alice Dal Fovo, Enrico Pampaloni, and Raffaella Fontana

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Spectral imaging and archival data in analysing *Madonna of the Rabbit* paintings by Manet and Titian

J. Striova*[a], C. Ruberto[b], M. Barucci[a], J. Blažek[c], D. Kunzelman,[d] A. Dal Fovo[a], E. Pampaloni[a] and R. Fontana[a]

Abstract:

A concise insight into the outputs provided by the latest prototype of visible-near infrared (VIS-NIR) multispectral scanner (National Research Council-National Institute of Optics, CNR-INO, Italy) is presented. The analytical data acquired on an oil painting *Madonna of the Rabbit* by É. Manet are described. In this work, the VIS-NIR was complemented with X-ray fluorescence (XRF) mapping for the chemical and spatial characterization of several pigments. The spatially registered VIS-NIR data facilitated their processing by spectral correlation mapping (SCM) and artificial neural network (ANN) algorithm respectively for pigment mapping and improved visibility of *pentimenti* and of underdrawing style. The data provided several key elements for the comparison with a homonymous original work by Titian studied within the ARCHive LABoratory (ARCHLAB) transnational access project.

The origin of Infrared reflectography (IRR) dates back to the 1960s.[1] Starting from 2000, the research focused on developing 2D scanning technique combining spectral data and areal information, by using multispectral and hyperspectral cameras.[2-5] Since then a single wide-band IRR has evolved into the multi-/hyperspectral imaging: a non-invasive, attractive and versatile method applied also in the field of heritage science. In the last decades, significant progress has been made in developing hyperspectral devices providing high-resolution image-cubes. Nevertheless, the considerable diversity of materials and stratigraphy in works of art makes their study inherently challenging.[6,7] The most advanced scanning devices for visible near-infrared reflectance imaging cover a 400-2500 nm range.[8,9] Cucci et al.[10] have recently surveyed the hyperspectral sensor systems, based on line spectrographs, reporting significant examples of reflectance imaging spectroscopy applications in cultural heritage. Dooley et al.[11] demonstrated the complementarity of reflectance and XRF spectroscopic imaging in identification and mapping the pigments in Renaissance paintings. The binders can be classified with the high resolution reflectance spectroscopy in the wavelength region above 2000 nm.[8] Moreover, the potential of multimodal (reflectance, luminesce and XRF spectroscopy) imaging with co-registered data in analysis of Greco-roman painting has been validated.[12] Alfeld and de Viguerie reviewed developments of the spectroscopic imaging methods and advantages in their joined use for the analyses of historical paintings.[8] An alternative to line scanning previously mentioned, a single point detection with catoptric optics enables the acquisition of aberration free images (multispectral imaging) and low-resolution spectroscopy. The current prototype, used here, exploits the latter principle with simultaneous acquisition in visible and near-infrared range through a single module. This device is an improvement of the previously constructed systems described by Bonifazzi et al.[13] and Daffara et al.[14] For detailed instrumental specifics, please refer to the supporting information.[SI] Several examples of the outputs obtained with such a device are shown here.

In this paper, we report on a methodology to investigate artworks that exploits analytical data acquired in laboratory with those available from archives. Such methodological approach may be very challenging as the comparative evaluation is based on data obtained in diverse context and periods and with partially different techniques. In this respect, the IPERION CH ARCHLAB platform, providing specialised knowledge and organized scientific information – including technical images, analytical data and conservation documentation, was accessed following a positive peer-review evaluation of proposal for a trans-national access

Figure 1. Painting by Titian©C2RMF a) RGB image, c) FC infrared photography; Painting by Manet b) RGB image after cleaning, d) FCIR (900-1000 nm+R+G).

Two homonymous oil on canvas paintings by Titian and Manet (Fig. 1a and 1b, resp.) entitled *The Virgin and Child with Saint Catherine and a Shepherd,* known as *Madonna of the Rabbit,* were examined in this context. Titian realized the original

[a] J. Striova, M. Barucci, A. Dal Fovo, E. Pampaloni, R. Fontana
National Research Council (CNR)-National Institute of Optics (INO)
Largo Enrico Fermi 6, 50125, Florence, Italy
E-mail: jana.striova@ino.cnr.it
[b] C. Ruberto,
Department of Physics and Astronomy, University of Florence
National Institute of Nuclear Physics (INFN)
Via Sansone 1, 50019 Sesto Fiorentino (FI), Italy
[c] J. Blažek
Institute of Information Theory and Automation
Czech Academy of Science
Pod Vodárenskou věží 4, 18208, Prague, Czech Republic
[d] Private practice, formerly Opificio delle Pietre Dure di Firenze, Italy

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version (71x85.5 cm) between 1525 and 1530, whereas Manet painted a copy (69.8x84.2 cm) around 1856.[SI] Manet's painting was analysed with visible near-infrared multispectral and XRF scanners during its restoration in Florence in 2016. [SI] Information on Titian's work, instead, was obtained from the archive at the Centre de Recherche et de Restauration des Musées de France (C2RMF) accessed in 2017.[15] The aim of this work was to compare and analyse inhomogeneous datasets referred to the above-mentioned artworks.

To highlight the differences in the constituting materials with focus on the blue pigments, the two paintings by Manet and Titian were compared based on the available data, acquired in laboratory and those from archive[15,16,17]. In particular, their false colour infrared images (FCIR) were examined. FC trichromatic RGB image of Manet's painting (Fig. 1b) was generated with 950 nm scanner reflectograms (FWHM = 100 nm) to provide a response as similar as possible to FC infrared photographic image available for Titian's painting (Fig. 1c), (max. 1050-1100 nm sensitivity of CCD/CMOS sensors). From both FCIRs, the presence of different pigments can be hypothesized. In FCIR related to Titian's painting (Fig. 1c), the blue pigments appearing bright red (in the mountain and in the Virgin's cloak) and purple/blue (the clouds in the sky and in St. Catherine's scarf) can be distinguished, suggesting the use of pigments with respectively high and low reflectance for 950 nm infrared radiation. Considering blue pigments available in Titian period, lapis lazuli and azurite come into consideration. In fact, due to the high reflectance for 950 nm infrared light, ultramarine appears light in infrared photography (bright red in FCIR), contrary to azurite.[18a] The reflectance spectra in the 400-800 nm range acquired on St. Catherine's shawl and the Madonna's cloak are reported in Fig. 2a and 2b for Titian and Manet, resp.

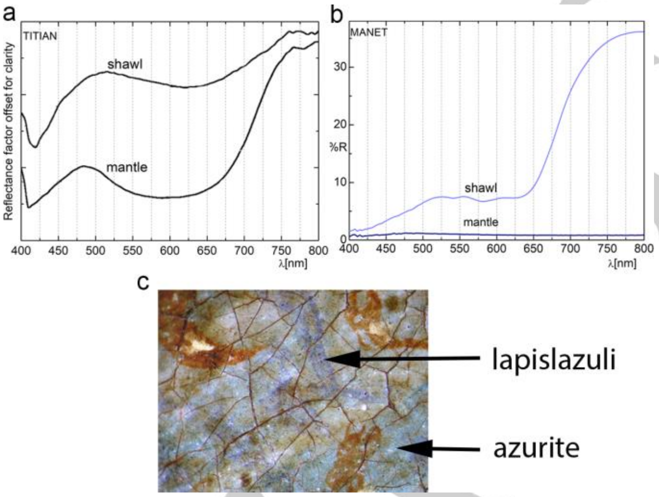

Figure 2. Reflectance spectra in 400-800 nm range on blue shawl and mantle for a) Titian©C2RMF, b) for Manet and c) microscopic image of the shawl (Titian)©C2RMF.

As inferred by the μXRF punctual analyses [16] revealing Cu, a Copper based pigment such as azurite ($2CuCO_3 \cdot Cu(OH)_2$) was used to realize St. Catherine's shawl. This would be confirmed by its reflectance spectrum with a strong absorption at 505 nm, weak transition at 607 nm, and at 847 nm, due to a combination of d-d and charge transfer transitions.[18a] However, the spectrum in Fig. 1h has contribution also from other compounds, such as ultramarine. The reflectance spectrum of natural ultramarine blue, chemically complex mineral pigment extracted from lapis lazuli, is characterized by absorption minimum at 600 nm (due to the charge transfer within the sulphur anions trapped in the alluminosilicate network).[18a] Moreover, the reflectance values result higher in red than in the blue region, feature typical of natural ultramarine.[19] Such spectrum may be identified with that reported in Fig. 2a, acquired on Virgin's mantle. By combination of XRF, visible spectrophotometric analyses and microscopic observation, it may be summarized that Titian realized the different shades of blue with the use of lapis lazuli and azurite. Lapis lazuli was used for the Virgin's mantle and the mountains in the background. The sky is painted with azurite and certain areas of the clouds were also lightened with lapis lazuli. For the scarf, Titian used the two pigments: azurite as a base and lapis lazuli over it (Fig. 2c).[16]

The reflectance spectra (Figs. 2b, 3a) acquired on St. Catherine's shawl (Manet) with both the high resolution punctual FORS (full line) and the VIS-NIR scanner (dots) exhibit two absorbance bands (550-650 nm and 1200-1550 nm). Each of the bands, subdivided into three smaller bands, as visible in FORS spectra, is related to the ligand-field occurring among the *d* orbitals of the Co^{2+} ion in a pseudo-tetrahedral coordination with four oxygen atoms. Such spectrum can be ascribed to the Cobalt blue ($CoO \cdot Al_2O_3$).[18b, 20, SI] This result is confirmed by XRF analysis which detects mainly Cobalt (Co-Kα line at 6.9 keV, Fig. 1c and S8) and not Si, Ni and As X-ray lines attributable to smalt. A characteristic X-ray Tin line (Sn-Lα at 3.4 keV) was not detected, suggesting the absence of Cerulean blue ($CoO \cdot nSnO_2$) (introduced as an artists' pigment after 1860[21]). The latter would also have the absorption bands shifted to higher wavelengths. [20] The reflectance spectra related to the Madonna's dark blue mantle (Figs. 2b, 3a) matched the reference of Prussian blue ($Fe_4[(Fe(CN)_6])$[18c], not featuring absorption bands, low reflectance values in visible range with gradual increase in %R values from about 1100 nm (inflection point at 1260 nm). The blue mantle was mainly characterized by iron signal (Fe-Kα at 6.4 keV), whose distribution map pinpointed the brushstrokes (Figs. 3c and S7). These results are in line with those reported in literature. Amato et al.[22] shows that Manet used Cobalt and Prussian blues in *Déjeuner sur l'herbe* (1863-8), a painting almost coeval with *Madonna of the Rabbit.* Instead, Cerulean blue was detected in Manet's paintings *Banks of the Seine at Argenteuil* (1870-1880) and *A Bar at the Folies–Bergère* (1882), along with the two aforementioned pigments.

The spectral correlation map[SI] (SCM, Fig. 3b), computed on VIS-NIR dataset before cleaning, shows the distribution of the Cobalt blue, coded in periwinkle colour. The map reveals its dominant presence in St. Catherine's shawl. It is also evidenced in dark zones (e.g., the animal held by the shepherd, the shepherd's hair, the wooden wheel St. Catherine is kneeling on), added probably to obtain a cool tone.[23] A several cm wide stripe in the perimeter (top left and upper edge) of the painting, related to the restoration intervention, similarly correlates with Co blue. This pigment was detected in several zones of pictorial lacunas (e.g., centre of the mountain behind St. Catherine's head and a narrow strip in the sky left of the mountain), suggesting its function as an underlayer. The SCM (Fig. 3b) shows the distribution of the Prussian blue (PB), codified in blue colour. It is evident that PB is a dominant pigment for the Madonna's cloak as well as for the mountains and sky, where it is probably laid over the Co blue. PB is also disclosed in the lawn in the foreground and other greenish zones throughout the painting.

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Figure 3. Manet: a) FORS (full line) and scanner (dots, triangles) reflectance spectra of blue shawl and mantle, b) SCM of blue pigments: Cobalt blue codified in periwinkle, Prussian blue in electric blue colour, c) XRF Co and Fe maps as referenced on 10x10 cm areas.

The FCIR (Fig. 1d) of Manet's painting, confirms the finding of spectral and XRF imaging. The Madonna's blue cloak appears dark because of the low reflectance of Prussian blue pigment whereas the Saint Catherine shawl appears bright pink due to the moderate reflectance at 950 nm of cobalt blue.

This project also sheds light on some choices Manet could have made during the realization of the painting. For example, one has to consider that at the time Manet reproduced the painting, around 1856, some colours of Titian's painting probably appeared differently than they do today, after its most recent restoration.[24] The green colours evident today in Titian painting (Fig. 4a,b) may have appeared brownish, due to the presence of oxidized varnish and/or the alteration of copper green pigment (e.g., verdigris or copper resinate) as single spot XRF measurements, performed in two green zones, both detected Cu.[17] Instead, the pigment used for the trees and most of the background in Manet's painting (Figs. 4c,d) was identified and mapped as ochre (Figs. 4e,f and S4b). The reflectance spectra exhibit two absorbance bands at 654 and 862 nm, attributable to the electronic transfer of Fe^{3+}. A high intensity of iron X-rays, combined with low intensity of potassium and titanium X-rays, confirm the presence of ochre in the brownish background. This is an evidence that Manet reproduced the foliage of Titian's painting with a yellow-brownish tone instead with a green pigment, as expected.

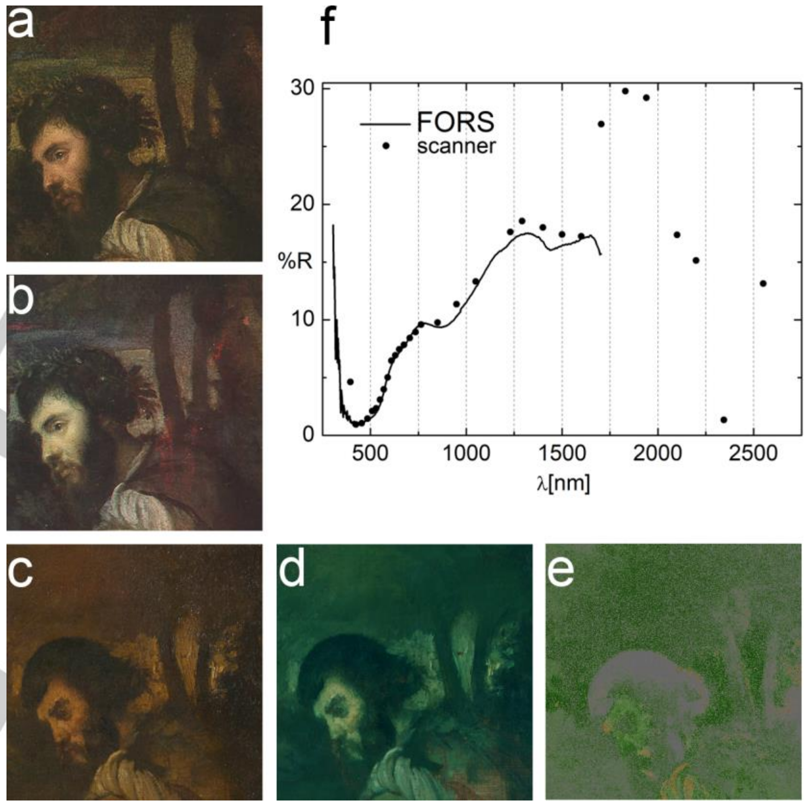

Figure 4. Detail of shepherd (10x10 cm) by Titian©C2RMF a) RGB image, b) FC photography image; by Manet c) RGB image, d) FCIR (900-1000 nm+R+G), e) spectral correlation map of yellow ochre, f) reflectance spectrum of brownish trees (FORS full line, scanner dots).

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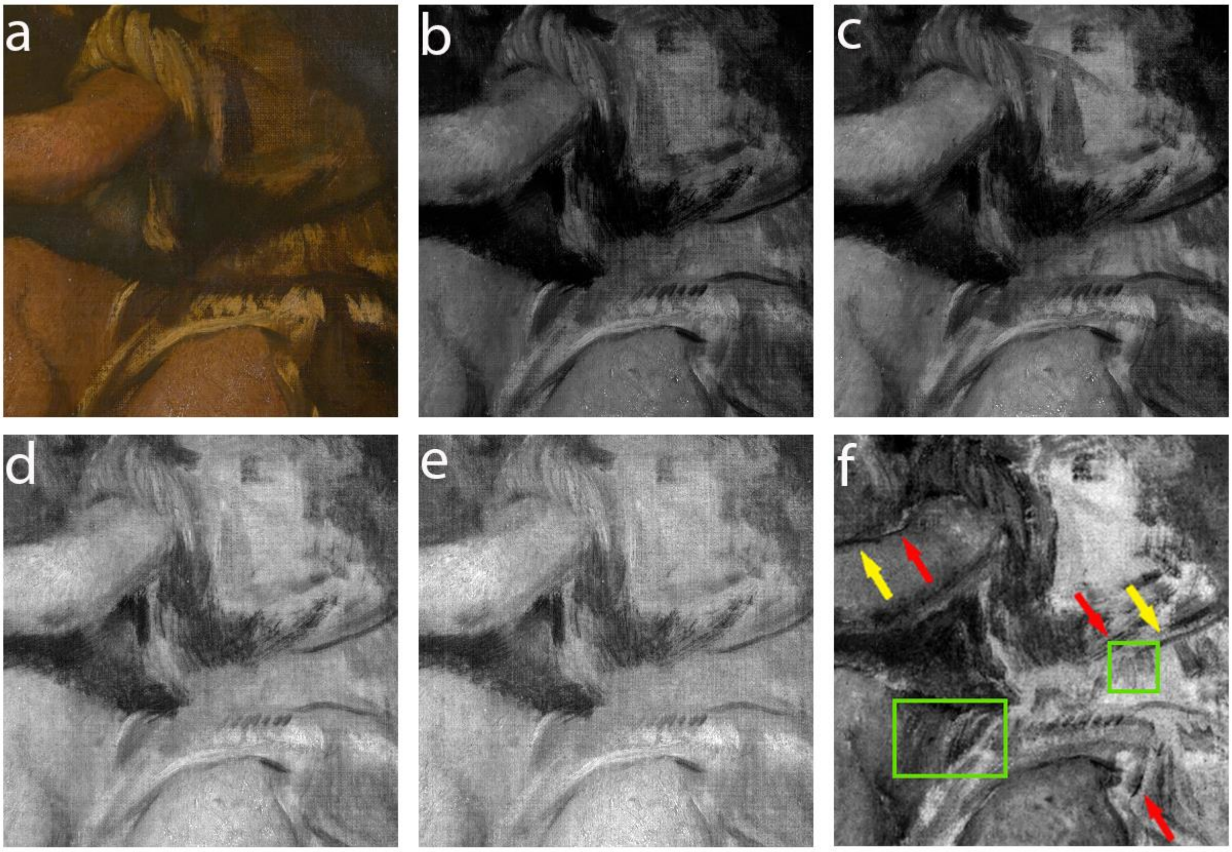

Figure 5. Detail of shepherd by Manet (9.6 x 10.0 cm): a) RGB image; b-e) reflectograms (resp. λ = 1050, 1400, 1700, 1940 nm); f) information gain by ANN (difference of extrapolated and measured reflectogram at λ=1400 nm). Red and yellow arrows mark the dry and wet drawing media, respectively; the green rectangles highlight the brushstrokes hardly visible in the reflectograms.

The VIS-NIR dataset was used to examine the technique Manet used to realize his work. A feed forward artificial neural network (ANN) algorithm[25], based on suppressing VIS information content from that contained in NIR, was applied to process the data collected on the selected regions of the painting to improve visualization of the underdrawing features. An example is reported in Figure 5 showing respectively the measured reflectograms and the result of the aforementioned digital processing. Details that appear/disappear by varying the wavelength (Fig. 5b-e) are summed up in the ANN image, e.g. the brushstrokes highlighted by the left green rectangle (Fig. 5f), whereas the small one shows a particular hardly discernible just at 1050 nm. The raw and elaborated data allow the visualization of the minimal preparatory phase with dry and wet drawing media with different appearance: the former thin and sharp, the latter thick and fluid (red and yellow arrows, respectively). It can be hypothesised that the specific nature of the artwork, which is a faithful copy of a painting that Manet directly observed, did not require particularly detailed drawing. Small changes in figure profiles (the head of Saint Catherine) and/or repositioning of elements (the rabbit) were realized mainly in the painting phase (Fig. S6).

The painting by E. Manet has recently joined the rooms of the Louvre museum, alongside the original by Titian, according to the last will of the painting's legatee. The preliminary results reported here form a sound basis for a more in-depth research that will further highlight the unexplored features related to both paintings. The comparative study demonstrates that not only the palettes used by the two authors were different, as might be expected, but also that the colours of the two paintings differ. The Manet's palette of pigments is in perfect agreement with the materials commonly used in the middle of the 19th century (such as Prussian and Cobalt blues, Cadmium and Zinc yellows, ochres, cinnabar, tin-based lake) as opposed to that of Titian (e.g., azurite, natural ultramarine blue, orpiment and lead-tin yellow). The aspects to address in the future may be aimed at understanding whether the painter's technical decisions were tied to the state of conservation of Titian's work at the precise moment when Manet copied it.

Experimental Section [SI]

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COMMUNICATION

Mapping blue pigments in Manet's painting *Madonna of the rabbit* (copy of Titian's homonymous painting) by spectral correlation of VIS-NIR multispectral data complemented with XRF mapping.

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