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

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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 identified 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 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. Two homonymous oil on canvas paintings (Fig. 1a and 1f) entitled The Virgin and Child with Saint Catherine and a Shepherd, known as Madonna of the Rabbit, were examined. Titian realized the original 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) in 2017. [15] The aim of this work was not only to compare the materials used by the two artists, but also to examine certain choices made by Manet when painting his version, for example the use of brown colours in the vegetation.

The analyses were first focused on the blue pigments. The reflectance spectra (Fig. 1b) acquired on St. Catherine's shawl (Manet) with both the VIS-NIR scanner (dots) and high resolution punctual FORS (full line) 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 ($CoO \cdot Al_2O_3$).[16, 17a, SI] This result is confirmed by XRF analysis detecting Cobalt (Co-Kα line at 6.9 keV, Fig. 1c and S8). A characteristic X-ray Tin line (Sn-Lα at 3.4 keV) was not detected, suggesting the absence of Cerulean blue ($CoO \cdot nSnO_2$). The latter would also have the absorption bands shifted to higher wavelengths. [16] This pigment was probably introduced as an artists' pigment after 1860. [18] The reflectance spectra related to the Madonna's dark blue mantle (Fig. 1b) matched the reference of Prussian blue ($Fe_4[(Fe(CN)_6])$ [17b], 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 (Fig. 1c and S7).

These results are in line with those reported in literature. The study by Amato et al.[19] 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.

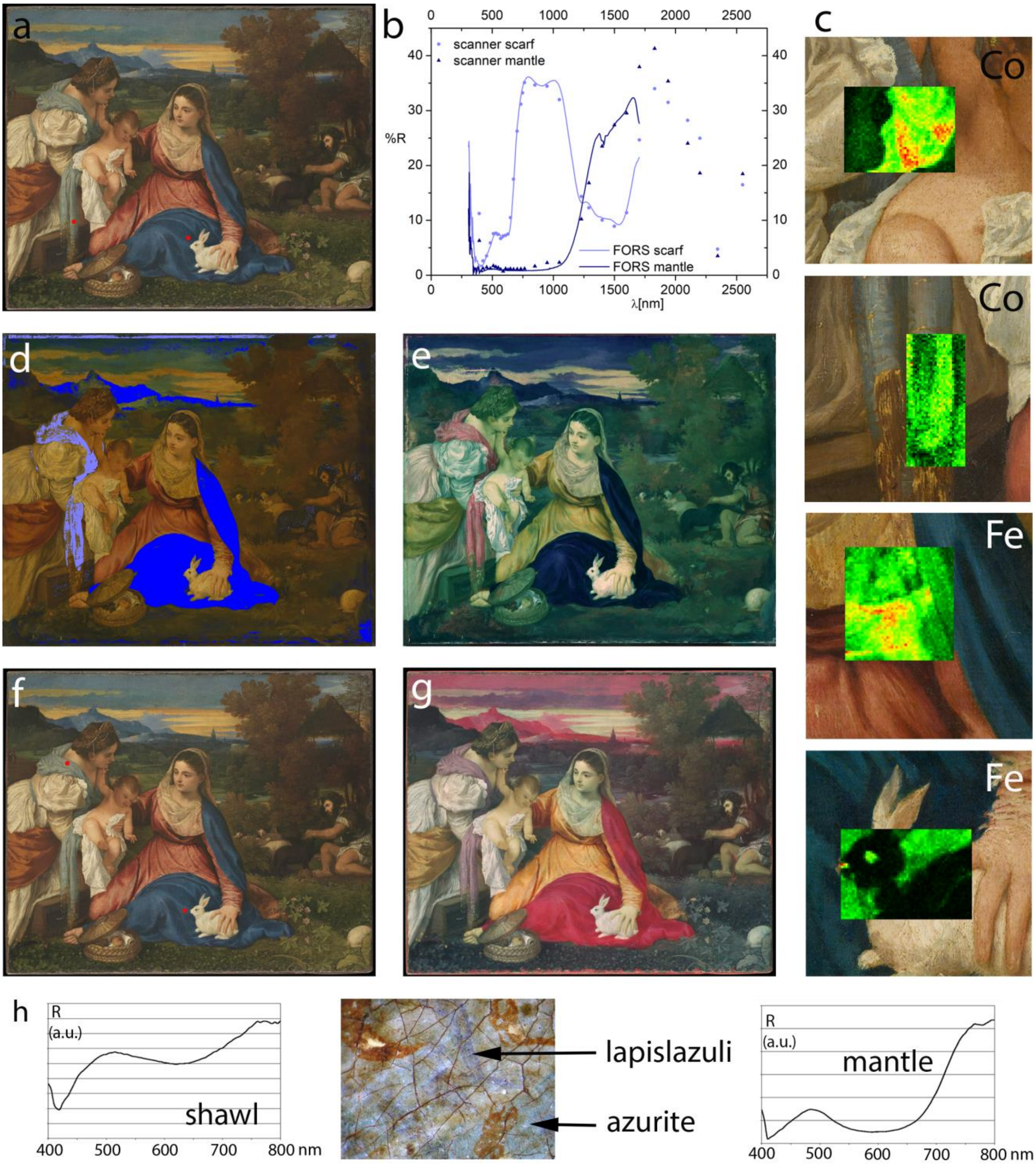

Figure 1. Painting by Manet a) RGB image after cleaning, b) reflectance spectra of blue pigments, c) XRF maps of Co and Fe on the shawl and mantle as referenced on a 10x10 cm area, d) SCM of blue pigments, e) FCIR (950nm+R+G); Painting by Titian © C2RMF f) RGB image g) FC infrared photography h) reflectance spectra in visible range acquired on shawl, h) microscope image of the shawl, i) reflectance spectra in visible range acquired on Virgin's cloak.

The spectral correlation map[SI] (SCM, Fig.1d), 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. [20] 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 same SCM image (Fig. 1d) 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.

To highlight the differences in the constituting materials, the two paintings by Manet and Titian were compared based on the available data, acquired in laboratory and those from archive[15,21,22]. In particular, their false colour infrared images (FCIR) were examined. FC trichromatic RGB image of Manet's painting was generated with 950 nm scanner reflectogram (Fig. 1e) to provide a response as similar as possible to FC infrared photographic image available for Titian's painting (Fig. 1g), (max. 1050-1100 nm sensitivity of CCD/CMOS sensors). The reflectance spectra in the 400-800 nm range acquired on St. Catherine's shawl and the Madonna's cloak are reported in Fig. 1h for Titian.

From both FCIRs, the presence of different pigments can be hypothesized. In FCIR related to Titian's painting (Fig. 1g), 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.[17c]

As inferred by the μXRF punctual analyses [21] revealing Cu, a Copper based pigment such as azurite (2CuCO3·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. [17c] 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). [17c] Moreover, the reflectance values result higher in red than in the blue region, feature typical of natural ultramarine.[23] Such spectrum may be identified with that reported in Fig. 1h, 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 have also been lightened with lapis lazuli. For the scarf, Titian has used the two pigments: azurite as a base and lapis lazuli over it. [21]

For Manet's painting, the FCIR (Fig. 1e) 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.

The project aimed at shedding further light on the choices Manet 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. The green colours evident today in Titian painting (Fig. 2a,2b) may have appeared brownish, due to the presence of oxidized varnish and/or the alteration of copper resinate that we hypothesize Titian used as a green pigment. In fact, the pigment used for the trees and most of the background in Manet's painting (Fig. 2d,e) was identified and mapped as ochre (Fig. 2c,f and S4b), with the two absorbance bands at 654 and 862 nm, attributed to the electronic transfer of Fe^{3+}. A high intensity of iron X-rays, combined with low intensity of potassium and titanium X-rays, the use of ochre confirm 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.

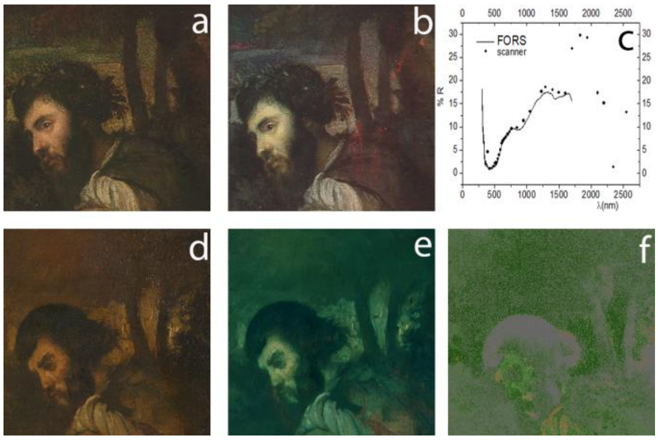

Figure 2. Detail of shepherd (10.0 x 10.0 cm) by Titian© C2RMF a) RGB image, b) FC photography image; by Manet c) reflectance spectrum of brownish trees d) RGB image, e) FCIR (950 nm+R+G), f) spectral correlation map of yellow ochre.

The VIS-NIR dataset was used to examine the technique Manet used to realize his work. A feed forward artificial neural network (ANN) algorithm[24], 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 3 showing respectively the measured reflectograms and the result of the aforementioned digital processing. The data reveal the minimal preparatory phase with dry and wet drawing media. 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).

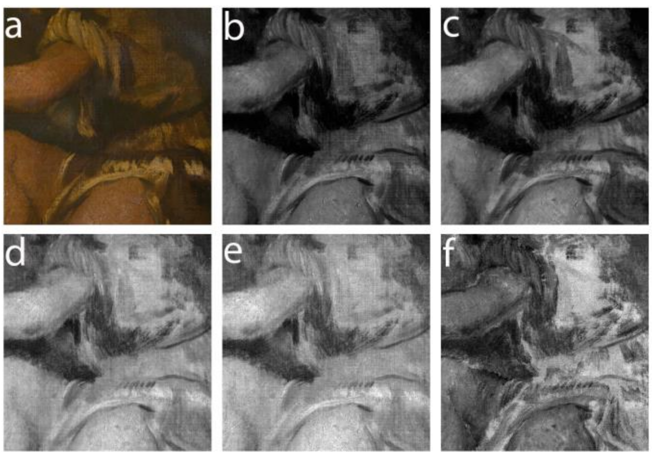

Figure 3. Detail of shepherd by Manet (9.6 x 10.0 cm): a) RGB image; b-e) reflectograms (resp. λ= 1050, 1400, 1700, 1940 nm); f) information gain by ANN (difference of extrapolated and measured reflectogram at λ=1400 nm).

The painting by E. Manet has recently joined the rooms of the Louvre museum, alongside the original, 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 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

Multispectral analysis was carried out by a scanner developed by INO-CNR with 32 spectral channels (16 in the visible (380 – 780 nm) and 16 in the near-infrared range (750 – 2500 nm). It consists of the XY(Z) scanning system that moves both the lighting and collecting systems placed in 45°/0° geometry and of a laser-based autofocus system (Z axis), keeping the working distance of approximately 12 cm. To avoid the chromatic and optical aberration, a catoptric system is used to collect the scattered radiation that is then focused on a square-shaped bundle of 36 optical fibres and carried to the detector array composed of Si and InGaAs photodiodes. Areas up to 1 m2 in one acquisition can be measured with a spatial sampling of 250 µm (~ 4 points/mm). The algorithm for improved visibility of underdrawing has been described elsewhere. [24]

XRF scanner developed at LABEC (Laboratory of Nuclear Techniques applied to Cultural Heritage), within the CHNet (Cultural Heritage Network) of INFN, consists of a measuring head composed of an X-ray tube, a detector and a telemetry system mounted on three stages. The probe is constituted by a lightweight and small Cr-anode X-ray tube (Moxtek MAGNUM®), with a 127µm Be exit window, 40 kV maximum voltage and 100 µA maximum anode current. Beam dimensions are defined by lead collimator with a 400 to 1500 µm aperture (800 µm in this work). The X-rays are collected by a SDD detector (XR100 SDD - Amptek©), with 17 mm2 collimated active area and processed by custom electronics. In our set-up, the probe and detector were positioned at about 45°. The three-axis precision positioning stages (PI/M-404.PD Physik Instrumente©) have travel ranges respectively 200, 200 and 50 mm in x, y and z. The x- and y- axes allow for the scanning motion, while the z- axis maintains automatically constant the distance from the target, through a dynamic positioning system for safe analyses on non-planar sample geometries. The spectral acquisition (20 kV anode voltage, 100 µA filament current, 1mm/s scanning velocity and 1x1 mm2 pixel dimension) and data analysis are controlled via custom open-source software.

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[1] J. R. J. Van Asperen de Boer Appl. Opt. 1968, 7(9), 1711–1714

[2] M. Kubik, in Physical techniques in the study of art, archaeology and cultural heritage; Creagh, D.; Bradley, D., Eds.; Elsevier Science: Amsterdam, 2007; Vol. 2, Chapter 5, pp 199–271.

[3] C. Balas, P. Vapadakis, N. Papadakis, A. Papadakis, E- Vazgiouraki, G. Themelis, J. Cult. Herit. 2003, 4, 330–33710.1016/S1296-2074(02)01216-5

[4] J. K. Delaney, J. G. Zeibel, M. Thoury, R. Litteton, K. M. Morales, M. Palmer, E. Renéde la Rie, in O3A: Optics for Arts, Architecture, and Archaeology II. Proc. SPIE 7391; Pezzati, L., Salimbeni, R., Eds.; SPIE: Munich, 2009; pp 739103−739103-8.

[5] M. Picollo, M. Bacci, A. Casini, F. Lotti, M. Poggesi, L. Stefani, in Proc. Conservation Science, Milan, May 10−11, 2007; Townsend, J., Toniolo, L., Capitelli, F., Eds.; Archetype Publications: London, 2008; pp 162−168.

[6] C. Cucci, M. Picollo, L. Chiarantini, B. Sereni, in Optics for Arts, Architecture, and Archaeology V. Proc. SPIE 9527; Pezzati, L., Targowski, P., Eds.; SPIE: Munich, Germany, 2015; pp 95270P-1−95270P-9

[7] H. Liang, Appl. Phys. A: Mater. Sci. Process. 2012, 106 (2) 309–32310.1007/s00339-011-6689-1

[8] M. Alfeld and L. de Viguerie, Spectrochem. Acta B, 2017, 136, 81-105

[9] K. A. Dooley, S. Lomax, J. G. Zeibel, C. Miliani, P. Ricciardi, A. Hoenigswald, M. Loew, J. K. Delaney, Analyst, 2013, 138, 4838

[10] C. Cucci, J.K. Delaney, M. Picollo, Acc. Chem. Res., 2016, 49, 2070-2079

[11] K. A. Dooley, D. M. Conover, L. Deming Glinsman, and J. K. Delaney,

Angew. Chem. Int. Ed. Engl. 2014, 53, 13775

[12] J. K. Delaney, K.A. Dooley, R. Radpour, I. Kakoulli, Sci Rep., 2017, 7: 15509

[13] C. Bonifazzi, P. Carcagni, R. Fontana et al. J. Opt. A: Pure Appl. Opt. 2008, 10, 064011

[14] C. Daffara, E. Pampaloni, L. Pezzati, M. Barucci, R. Fontana, Acc. Chem. Res. 2010, 43, 847-856

[15] Ruberto et al. ARCHLAB transnational access. Project Proposal TiMaRabbit, C2RMF archives accessed 31/05 - 2/06/2017

[16] M. Bacci, D. Magrini, M. Picollo, M. Vervat, J. Cult. Herit., 2009, 10, 275–280

[17] a) A. Roy (Cobalt Blue) in Artist's pigments, Vol. 4 (Ed. E. W. FitzHugh), National Gallery of Art, 2007, pp. 151-177; b) B. H. Berrie (Prussian Blue) in Artist's pigments, Vol. 3 (Ed. E. W. FitzHugh), National Gallery of Art, 1997, pp. 191-211; c) R. J. Gettens and E. W. Fitzhugh (Azurite) and J. Plesters (Ultramarine blue) in Artist's pigments, Vol. 2 (Ed. A. Roy), National Gallery of Art Washington, 1993, pp. 23-54

[18] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall in The pigment compendium

Elsevier Butterworth-Heinemann, 2004, p. 90

[19] S. R. Amato, A. Burnstock et al. X-ray Spectrometry in press

[20] D. Bomford and A. Roy in National Gallery Technical Bulletin Volume 7, 1983.

[21] B. Motin, M. Eveno, E. Laval, Compte-rendu d'etude du C2RMF: Titien (Tiziano Vecellio, dit) (1488/89-1567), La Vierge à l'enfant avec sainte Catherine d'Alexandrie, dite La Vierge au Lapin, Paris, muesée du Louvre (INV 743), 6.7. 2007, ref F5515a.

[22] Eric Laval, Microfluorescence X, Scientific report© C2RMF, 7.7. 2007, ref F5515b

[23] M. Aceto, A. Agostino, G. Fenoglio, M. Picollo, Anal. Methods, 2013, 5, 4184

[24] J. Blažek, J. Striova, R. Fontana, B. Zitová, Digit. Signal Process., 2017, 60, 140–151 http://dx.doi.org/10.1016/j.dsp.2016.09.007

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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.

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