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In Situ Noninvasive Study of Artworks: The MOLAB Multitechnique Approach

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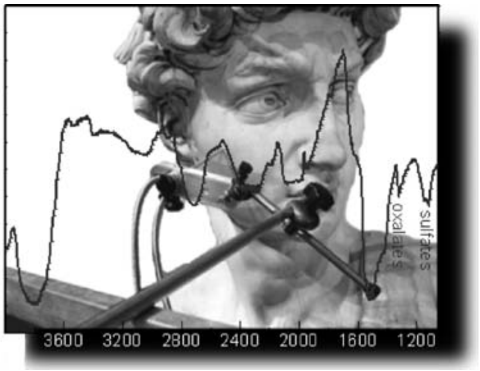

Driven by the need to study precious and irreplaceable artworks without compromising their integrity, researchers have undertaken numerous efforts to develop noninvasive analytical tools and methodologies that can provide a chemical description of cultural heritage materials without any contact with the object. The challenge is that artworks are made of complex mixtures, often with heterogeneous and unknown layered materials. Their components must be identified over a range of size scales, from the molecular identification of constituent compounds to the mapping of alteration phases.

In this Account, we review recent research in spectroscopic techniques accessible from the mobile laboratory (MOLAB). The lab is equipped with an array of state-of-the-art, portable, and noninvasive instruments specifically tailored to tackle the different issues confronted by archaeologists, curators, and conservators. The MOLAB approach is suitable for studying a variety of objects, from ceramics to manuscripts or from historical wall paintings to contemporary canvases.

We begin by discussing issues related to the acquisition and interpretation of reflectance or backscattered spectra from the surface of heterogeneous materials. Then we show how the selectivity needed for the noninvasive identification of pigments in paintings, even in mixtures or in layered matrices, can be acquired by combining elemental information from X-ray fluorescence with molecular and structural insights from electronic and vibrational spectroscopies. Discriminating between original pigments and restoration retouches is possible, even when both comprise similar chromophores, as highlighted in the study of paintings by Jordaens and Raphael. The noninvasive approach permits the examination of a very large number of artworks with a virtually limitless number of measurements. Thus, unexpected and uncommon features may be uncovered, as in the case of a lead pyroantimonate yellow doped with zinc that was discovered by micro-Raman and X-ray fluorescence on an Italian Renaissance majolica. For characterizing binding media, we discuss the strengths and limitations of using mid- and near-FTIR (Fourier transform infrared) spectroscopies supported by a multivariate statistical analysis, detailing the study of organic materials in a wall painting by Perugino and a survey of the painting technique on 18 contemporary paintings by Burri. In Michelangelo's David, we show how the noninvasive mapping of contaminants and alteration phases might inform decisions on preventive conservation plans.

The multitechnique MOLAB approach overcomes the intrinsic limitation of individual spectroscopic methods. Moreover, the ability to analyze artworks without the need to move them is an invaluable asset in the study and preservation of cultural heritage.

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1. Introduction

In recent decades, several advanced analytical methods have been successfully employed to investigate cultural heritage materials working on both minute bulk samples or cross sections. However, the use of microdestructive techniques reveals two main limitations. The first is the requirement of sampling that, although minimal, is not advisible when dealing with irreplaceable or precious items. Second, even in instances where microspecimens may even be available (typically from the edges or from damages or lacunae), the sampling sites may not be representative of the entire artwork.

To overcome these shortcomings, there has been a growing interest in the use of noninvasive analytical techniques able to yield information by remote examination of the entire artwork. In this context, we carry out our research activity aimed at setting up new spectroscopic tools and integrated methods for analyzing cultural heritage materials directly, without any contact with the surface of the object. In particular, in order to carry out noninvasive measurements in situ (i.e., in the same places where the artworks are exhibited or conserved), we moved toward the exploitation of portable equipment.

Bringing analytical equipment from the laboratory to the artwork, rather than the reverse, conveys particular advantages. Any risk (and costs) connected with the transportation of a high-value and fragile object into a lab is avoided, paving the way for the investigation of a very large number of artworks. The results are obtained practically in real time, creating a new form of relationship between scientists, conservators, and curators, based on immediate discussion of results.

The interest of the cultural heritage community for the noninvasive in situ approach is proved by the fact that research groups based in conservation institutes, such us the Getty Conservation Institute,[1] the Canadian Conservation Institute,[3] and the Centre de Recherche et de Restauration de Musées de France,[2] have assembled some analytical instruments to form portable laboratories in order to facilitate their research in artwork conservation.

In the present Account, we report on recent developments in optimizing instruments and methods of a mobile laboratory (MOLAB) made of an integrated suite of several spectroscopic techniques ranging from X-ray to near-infrared. We initially discuss relevant issues concerning the interpretation of spectral signals collected in reflectance or backscattering mode from heterogeneous matrices. Afterward, selected experimental results are detailed with the aim of highlighting actual performances of the noninvasive approach in the study of the chemical composition of different types of objects. Remarks concerning the current shortcomings, as well as possible developments, are also given in the conclusion.

2. Noninvasive Portable Equipment and the Multitechnique Approach

MOLAB is equipped with an array of state-of-the-art portable and noninvasive instruments for both point and imaging analyses. The spectroscopic point techniques, discussed in this Account, range from the X-ray to the IR region of the electromagnetic spectrum; their main characteristics in terms of portability, spectral parameters, spatial resolution, and probe–artwork distance are provided in Table 1. Most of the systems have been intentionally set up, using commercial optical and electronic components, selected by achieving the best compromise between efficiency and portability. They all are designed to be compactly transported as separate kits that can be assembled and aligned directly onsite (Figure 1).

TABLE 1. Main Technical Parameters of MOLAB Equipment for Spectroscopic Point Analysis[a]

technique	spectral range	spectral resolution	spatial resolution (mm^2)	dimension (cm^3)/weight (kg)	probe–artwork distance (mm)	experimental setup (excitation source/ detection system/sampling probe)
*XRF[4]	1.7–30 keV	150 eV (FWHM) at 5.9 keV	12	probe head: 40 × 40 × 30/3	20	W anode X-ray source/Si drift detector
micro-Raman[5]	250–2000 cm^{-1}	10 cm^{-1}	0.1	probe head: 20 × 10 × 10/0.5	15	Nd:YAG (532 nm) and diode (785 nm) laser/CCD/quartz fiber optic
mid-FTIR[6]	7000–900 cm^{-1}	4 cm^{-1}	12	50 × 50 × 50/35	4–8	globar source/MCT detector/chalcogenide glass fiber optic
*near-FTIR[7]	12500–4000 cm^{-1}	4 cm^{-1}	12	50 × 50 × 50/35	4–8	halogen lamp/InGaAs detector/quartz fiber optic
UV–vis reflectance[7]	250–850 nm	2 nm	10	30 × 20 × 20/10	2	deuterium-halogen lamp/CCD/quartz fiber optic
UV–vis fluorescence[8]	200–1100 nm	25 nm	2	30 × 20 × 20/10	4	xenon lamp/CCD/quartz fiber optic
TCSPT[9b]	350–850 nm	100 ps[c]	12	60 × 70 × 50/35	4	LED (455 nm) and diode (375, 650 nm) laser/photocathode detector/silica fused fiber optic

[a] Further experimental details are reported in the cited references. Asterisk indicates commercial equipment. [b] Time correlation single photon counting for fluorescence lifetime measurements. [c] Lifetime resolution.

FIGURE 1. On-site installation of the mobile facility MOLAB at the Statens Museum for Kunst, Copenhagen.[10]

The challenge of on-site noninvasive measurements arises from matrix effects, due to the fact that the spectral signals are generally collected in backscattering or reflectance mode from the surface of heterogeneous and often layered systems. Matrix effects convey different consequences for each spectroscopic method and must be carefully evaluated to obtain reliable information from spectral features.

Regarding X-ray fluorescence (XRF), the matrix effect leads to the loss of proportionality between intensity and concentration since the emission intensity of chemical elements is affected by the overall composition of the area under investigation.[11,12] Some attempts have been recently reported on the quantitative interpretation of XRF spectra of favorable cases.[13,14]

Micro-Raman measurements from painting surfaces lead to a large interfering background generated by the luminescence of binders and varnishes.[15] To minimize this problem, a time-resolved Raman portable spectrometer has been recently developed,[16] while others have applied the subtracted shifted Raman spectroscopy method.[17]

Concerning UV−vis fluorescence, it has been recently shown that the luminescence, traveling through the paint, can be affected by several physical factors (i.e., self-absorption, multiple scattering, inner filter effects) resulting in shifts or even distortions of emission bands.[15,16] In the attempt to avoid such pitfalls, a correction method based on Kubelka−Munk theory has been recently optimized on both mock-ups and genuine artworks.[18,19]

Reflectance fiber optic mid-FTIR (Fourier transform infrared) measurements generally imply a normal optical layout (0°/0° geometry) and therefore the collection of both diffuse and specular reflection with a ratio that basically depends on the roughness of the object surface. The consequences of competitive components of reflectance lead to challenges in the spectral interpretation, as well illustrated in Figure 2. In particular, the specular reflection, governed by Fresnel's law, depends on both the absorption index (*k*) and refractive index

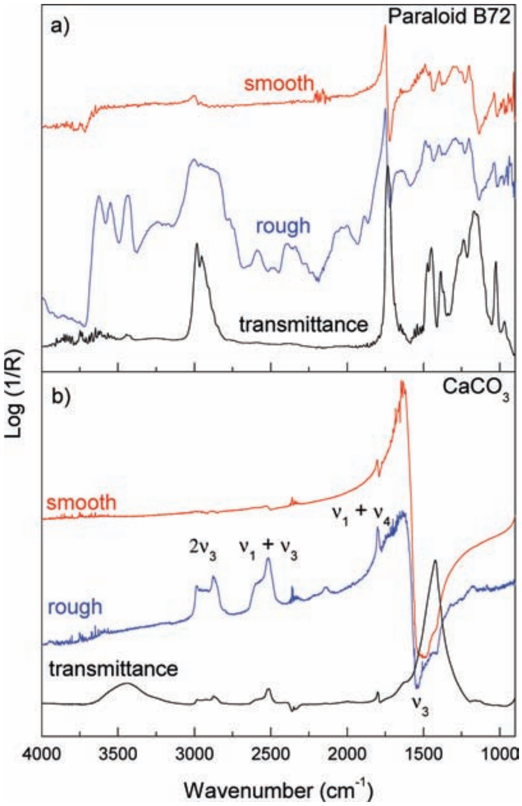

FIGURE 2. Reflectance mid-FTIR spectra collected on a smooth (red lines) and rough (blue lines) surface of (a) an acrylic film, Paraloid B72 and (b) $CaCO_3$. For comparative purposes, the respective transmission spectra are reported.

(*n*). Accordingly, organic compounds show derivative-like spectral features (Figure 2a), while spectra of minerals are often distorted by the inversion of those fundamental bands that show $k \gg n$ (*reststrahlen* effect, Figure 2b).[20] The diffuse reflection is ruled by Kubelka−Munk's law and depends on both the absorption index and scattering coefficient. The main distortion generated by diffuse reflection is the change of relative band intensities with respect to transmission mode. Weak absorption bands strongly increase in their intensity; thus, in reflectance mode, absorptions relative to minor components or combination and overtone bands of major components become visible (Figure 2).

The MOLAB approach for the integrated noninvasive study of a polychromatic artwork initially provides for a general survey using imaging methods (UV−vis fluorescence imaging and near-IR reflectography, not discussed in this Account) aimed at selecting specific areas of interest to tackle the issues posed by archeologists, curators, or conservators. The second step consists of a wide campaign of XRF measurements, followed by molecular spectroscopies: first, mid- and near-FTIR (for inorganic pigments and binders) and then UV−vis absorption and emission (for organic pigments). Afterward, micro-Raman measurements (for inorganic pigments) are usually attempted in the case of low fluorescing objects (i.e., ceramics and manuscripts).

3. In Situ Experimental Results

In the past few years, we have been involved in several research projects studying over two hundred artworks: from marble sculptures[21] (by Michelangelo, Antelami, Canova, etc.) to wall paintings[22−24] (by Perugino, Gaddi, Lippi, etc.), from ancient easel paintings[10,19,25,26] (by Raphael, Mantegna, Bronzino, Vasari, Jordaens, etc.) to modern and contemporary canvases[4,7,27] (by Cezanne, Renoir, Rothko, Munch, Burri, etc.), and from ceramics[5,28] (Renaissance Italian and early Meissen lusterwares) to manuscripts[9] (*Book of Kells*, *Codice Cospi*, etc.). The activity has been executed in Italy, within national projects, as well as in Europe, within the transnational access service offered to European researchers through the Eu-ARTECH and CHARISMA projects.[29]

3.1. Noninvasive Identification of Pigments. The identification of pigments used to paint works of art is fundamental to further the understanding of an object's history or an artist's technique, and may provide evidence for dating or attribution. Characterization of the artist's original colored materials as well as materials applied later (by artists or restorers) is important for providing criteria for an optimal conservation.

TABLE 2. List of the Most Used Organic and Inorganic Blue Pigments from Antiquity to 19th Century[a]

name	formula	period[32]	technique[b]
indigo	$C_{16}H_{10}N_2O_2$	antiquity	UV−vis fluo[8,9] and FTIR
egyptian blue	$CaCuSi_4O_{10}$	antiquity	UV−vis fluo[33] and FTIR
azurite	$2Cu(CO_3)\cdot Cu(OH)_2$	antiquity	XRF and mid-FTIR[22]
lapis lazuli	$Na_{7.5}[Al_6Si_6O_{24}]S_{4.5}$	antiquity	XRF and mid-FTIR[34]
smalt	$SiO_2(\mathit{vit})Co_x$	antiquity	XRF and near-FTIR[35]
Prussian blue	$M(I)Fe(III)[Fe(II)(CN)_6\cdot nH_2O]$	from ∼1720	XRF and mid-FTIR[22,28]
synthetic ultramarine	$Na_{7.5}[Al_6Si_6O_{24}]S_{4.5}$	from 1824	XRF and mid-FTIR[34]
Thenard's blue	$CoAl_2O_4$	from ∼1800	XRF and near-FTIR[4,7,30]
cerulean blue	$CoO\cdot n[SnO_2]$	from ∼1870	XRF and near-FTIR[30]

[a] MOLAB techniques used for their onsite noninvasive identification in paintings are provided. [b] Raman spectroscopy is not reported, since in easel paintings very often the scattering is hampered by fluorescence background from binders and varnishes.

Conversely, from other materials, there is rather ample literature on the exercising of a noninvasive and in situ approach to gather an insight into the chemical composition of colored compounds by means of a single analytical method, with XRF[11−14] and UV−vis reflectance[30,31] being the most commonly applied. On this basis, we developed a multitechnique strategy able to provide a description of molecular compositions comparable to that achievable from microdestructive conventional analyses.[7] Some examples of the MOLAB multitechnique approach for the pigment identification in easel paintings and ceramics are here discussed.

Blue Colors in Easel Paintings. The painting *The Ferry Boat from Antwerp* by Jacob Jordaens (c. 1623) was studied by MOLAB at the Statens Museum for Kunst in Copenhagen (Figure 1).[10] One of the questions addressed in the project concerned the distribution of blue pigments over the painting surface, since several different tonalities were visible. By the multitechnique approach, properly combining XRF data with those from UV−vis fluorescence, mid-FTIR, and/or near-FTIR, it is currently possible to noninvasively discriminate between the nine different compounds listed in Table 2.

Regarding Jordaens painting, five different compounds have been pinpointed alone, in mixtures or even layered. Smalt and indigo have been found on original areas such as on the woman's skirt (Figure 3). Jordaens used indigo as a dark underpaint highlighted by partially discolored smalt brushstrokes. The presence of smalt has been inferred on the basis of cobalt signals in the XRF spectra and near-FTIR evidencing the typical shape of the electronic absorption due to *d-d* transition of Co(II) in pseudotetrahedral coordination[35] (Figure 3a). Indigo has been ascertained on the basis of mid-FTIR rich features and the typical UV−vis fluorescence emission at about 730 nm (Figure 3b). These results have been confirmed

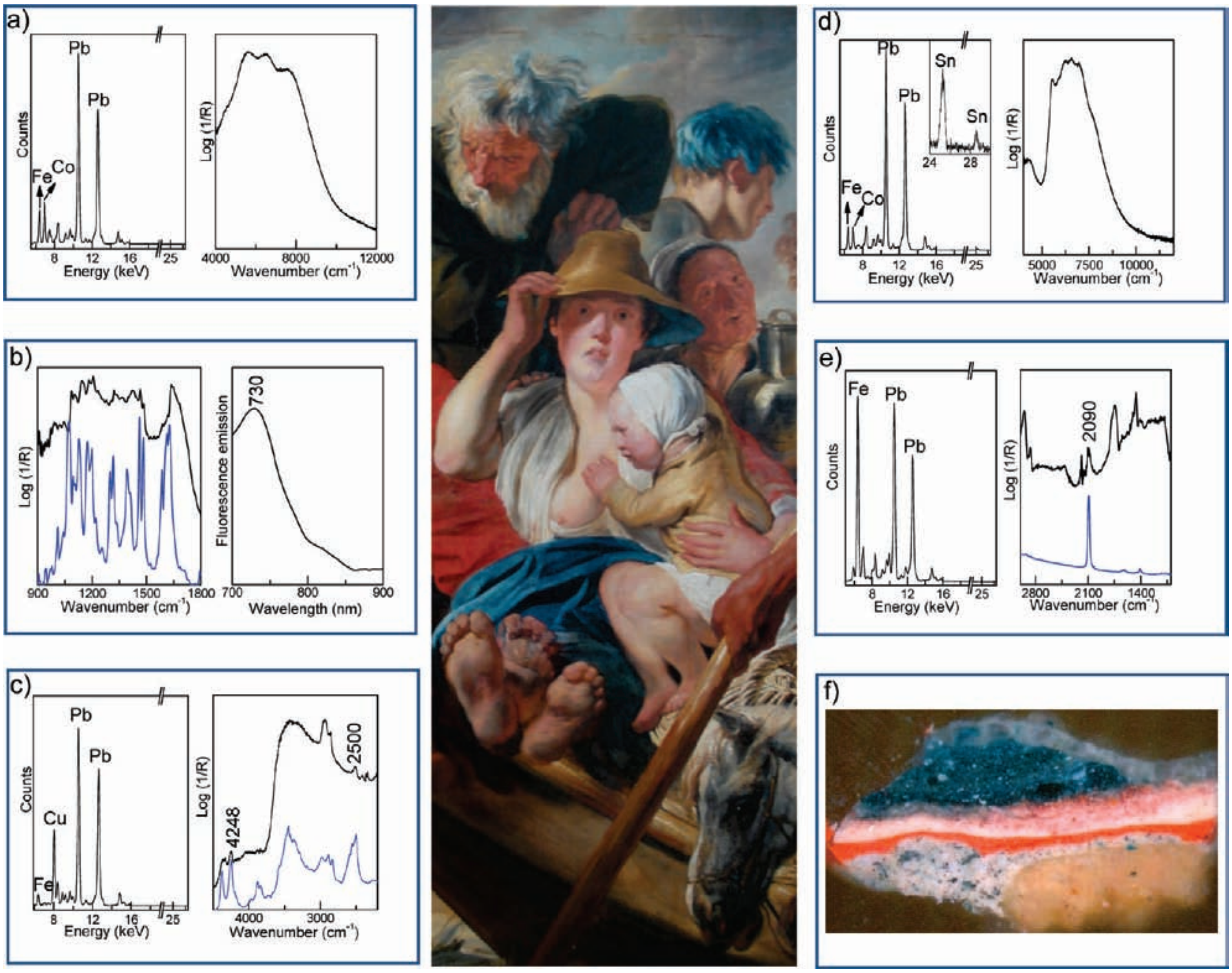

FIGURE 3. Study of blue pigments of *The Ferry Boat from Antwerp* (c. 1623) by Jordaens (detail of the painting is shown in the middle). In situ spectra (black lines) used for the identification of (a) smalt (left XRF, right near-FTIR); (b) indigo (left mid-FTIR, right UV−vis fluorescence); (c) azurite (left XRF, right mid-FTIR); (d) cerulean blue (left XRF, right near-FTIR), and (e) Prussian blue (left XRF, right mid-FTIR). Mid-FTIR spectra of references are reported for comparison (blue lines). Inset in (f) shows the optical image of a cross-section taken from the skirt of the woman on the boat.[10]

by the analyses of selected microsamples carried out by the museum conservators.[10] As an example, the optical image of a cross section from the woman's skirt is reported in Figure 3f, showing an upper thin layer of discolored smalt over a base of indigo.

Jordaens also used azurite to color both the sky and the sea, often mixed with malachite and lead white. Azurite has been identified through the presence of the copper signal in XRF and infrared combination bands of both the copper carbonate (at about 2500 cm^{-1}) and hydroxide (at about 4248 cm^{-1}) moieties (Figure 3c). The latter features permit the identification of azurite also when in mixture with malachite.[22] Beyond the original pigments, a further two blue compounds (cerulean blue and Prussian blue) have been revealed, assigned to previous retouches as these are not temporally compatible with Jordaens's period (Table 2). Cerulean blue has been distinguished from smalt by the signal of tin in XRF and by the different position and shape of the Co(II) electronic transition in the near-infrared (Figure 3d).[30,35] Prussian blue has been identified by the strong CN asymmetric stretching at 2090 cm^{-1} in the mid-FTIR spectrum[22,28] (Figure 3e) in small traces on the woman's skirt. The residual blue retouches are ascribable to the early restorations dating back to 1797−1884,[10] probably carried out to disguise the discoloration of smalt.

A similar issue has been addressed by MOLAB during the recent restoration of the *Madonna of the Goldfinch* by Raphael (c. 1506, Galleria degli Uffizi, Firenze). Conservators posed the problem to distinguish between early restoration materials and 19th century overpaints. In fact, the panel sustained severe damage only 40 years following its creation, when the owner's house was unexpectedly ruined; consequently, it was

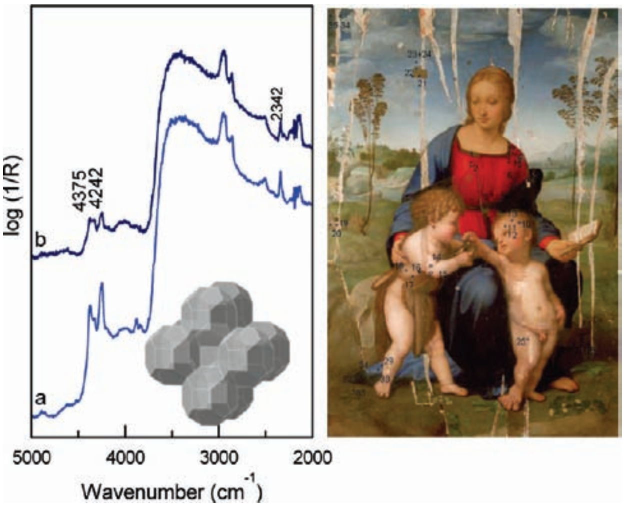

FIGURE 4. Study of the blue pigments featured in the *Madonna of the Goldfinch* (c. 1506) by Raphael. On the right, an image of the painting during the restoration process is shown (points refer to the measurement locations). On the left, mid-FTIR spectra recorded on the upper left part of the painting are shown (spectrum a corresponds to point 34, and spectrum b to point 35). Inset depicts the lapis lazuli chromophore structure made of sodalite β-cages containing CO_2 as well as $S_3^{\bullet-}$.[34]

restored for the first time by the painter Ridolfo del Ghirlandaio. Interestingly, noninvasive measurements proved that, for the reconstruction of damaged areas, Ridolfo used the same blue pigments originally employed by Raphael: lapis lazuli painted over a layer of azurite. In Figure 4, two mid-FTIR spectra are shown collected from areas of the sky, one painted by Raphael (spectrum a, point 34) and the other, at the extreme left-hand corner of the panel, painted by Ridolfo (spectrum b, point 35). Beyond the typical combination bands of azurite, both spectra have a sharp band at 2342 cm^{-1} that we proved to be due to the asymmetric stretching of CO_2 entrapped in the sodalite β-cages of lapis lazuli, from its geological genesis.[34] Diversely, the later retouches resulted to be made of smalt, Prussian blue, and synthetic ultramarine. This last one is the synthetic analogoue of lapis lazuli obtained by the furnacing of a mixture of kaolin, sulfur, and sodium carbonate. The two pigments share the same chromophore molecular structure (a sodalite framework containing the blue trisulfur radical anion, Figure 4) but can be differentiated since only the natural one retains traces of CO_2.[34] Encapsulated carbon dioxide can be straightforwardly identified by noninvasive mid-FTIR measurements through diffuse minor absorption band enhancement.[34]

Naples Yellows in Binary and Ternary Composition. In ceramics, pigments are applied as dispersed cations or crystalline phases embedded in transparent or opacified glazes. In this fashion, they can be conveniently analyzed on-site by exploiting portable micro-Raman.[36]

In this regard, we have been recently engaged in a wide study on Naples yellow and its modified forms in glaze Renaissance ceramics.[37] Naples yellow is one of the oldest known synthetic pigments, since its production goes back to about 3500 years ago; in Western European art, it has been used since the 16th century in Italian *majolica* and later in paintings. It consists of a lead antimonate oxide ($Pb_2Sb_2O_7$) displaying the cubic pyrochlore structure as depicted in Figure 5a. The interest for modified versions of Naples yellow arises from a study by Roy and Berrie that in 1998 discovered the ternary form $Pb_2Sb_{2\text{-}x}Sn_xO_{7\text{-}x/2}$[38] on Italian paintings of the 17th century. The existence of the modified pigment was later confirmed on a number of paintings from the 17th to the 19th century.[26,39] Very recently, during a MOLAB project on 11 Italian Renaissance *istoriato* wares belonging to the Victoria and Albert Museum, we disclosed a further ternary form of Naples yellow on an original plate from Castel Durante (1537) where tin was substituted with zinc.[5] The plate is shown in Figure 5b. The zinc modified pigment was used to color the bright orange stole of the boy, while the light yellow decorations on the background were depicted with the conventional lead pyrochlore (Figure 5c). In Figure 5d and e, XRF and Raman spectra collected on yellow and orange areas are compared. XRF graphs highlight the presence of tin (ascribable to cassiterite), lead, and antimony on both areas, while zinc is evidenced only on the orange one. The yellow decoration displays the typical Raman feature of Naples yellow, that is, a strong scattering at about 510 cm^{-1} related to the symmetric stretching of the SbO_6 octahedra.[37] The same Raman scattering mode in the orange decoration appears split in two bands, one again at 510 cm^{-1} and the other, less intense, at 450 cm^{-1}. On the basis of structural study on standards of lead antimony yellows, we proved this spectral feature distinctive of a doped pyrochlore with antimony partially substituted by zinc or tin.[37]

This experimental observation finds an explanation in historical records, considering what Piccolpasso suggested about producing the antimonate yellow: "...to make the most beautiful *zalulino* (i.e., Naples yellow) many add some *tutia allesandrina*, which is very good", where very likely *tutia* refers to zinc oxide as indicated by a long series of quotations in Western historical sources.[40]

3.2. Study of the Painting Technique: Binding Media Characterization. The binding media (basically proteins, glycosides, and lipids in ancient art, yet a wide range of synthetic polymers in contemporary art) with their own chemical-phys-

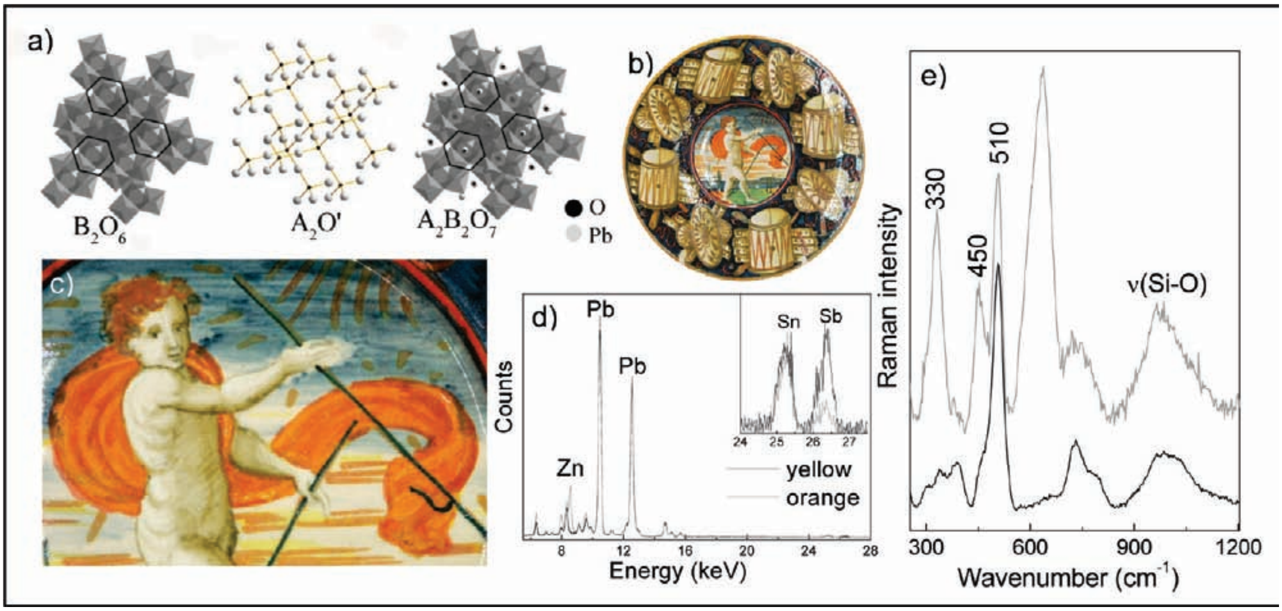

FIGURE 5. (a) Crystal structure of pyrochlore represented as two interpenetrating networks. The A_2O' network corresponds to four-coordinate O′ ions and two-coordinate Pb cations. The B_2O_6 framework consists of SbO_6 octahedra sharing all vertices to form large cavities.[37] (b) Image of plate 7688-61 from the V&A collection (1537). (c) Detail of the plate showing the orange stole and the yellow decorations on the back. (d) XRF spectra collected on the yellow (black line) and orange (gray line) decorations. (e) Raman spectra collected on the yellow (black line) and orange (gray line) decorations.

ical properties are the components that mostly affect the modus operandi of an artist. Even if there are benchtop analytical techniques that, on microsamples, may give detailed specification on a binder up to its biological origin, the value and benefit of a methodology able to noninvasively produce information on the binder's chemical class (proteins, lipids, etc.) are self-evident. To this purpose, we have recently set up a methodology for the on-site noninvasive binder characterization exploiting reflectance vibrational spectroscopy in the near-[27,41] and mid-[6,22,27] infrared region.

Organic Binders in Wall Paintings. The characterization of organic materials in wall paintings is particularly challenging due to their small amount with respect to the inorganic matrix (basically composed of lime-based plasters and pigments). To tackle this issue, we explored strengths and limitations of using the reflectance mid-FTIR technique supported by multivariate statistical analysis.[6] Specifically, we have constructed a model based on the principal component analysis (PCA) of reflectance spectra collected on hundreds of mocks-ups (painted with different binders and pigments) and then tested on a number of wall paintings by Perugino, Gaddi, and Lippi.

As an example, the t_1 vs t_4 score plot resulting from the PCA of a data matrix composed of spectra collected on mock-ups painted *a secco* with three different binders (casein, animal glue, whole egg) and *a fresco* with water is shown in Figure 6a. Application with water and casein are distinguished from applications with whole egg and rabbit skin glue. The possibility to differentiate between whole egg and animal glue depends on the amount of the lipid component in egg, whose carbonyl bond at 1740 cm^{-1} is not always well resolved from the *reststrahlen* band of calcium carbonate.

This PCA model has been tested on spectral data acquired on a wall painting by Perugino (*Adoration of the Magi*, 1521).[22] The painting is characterized by the presence of residues from an original *secco* overpaint that is appreciable in the UV-fluorescence image (see the damask decoration of the Wise King's gown, Figure 6c), while not visible in normal light. The univariate analysis of the spectra from the Wise King's gown highlighted the following: a proteinaceous binder showing strong signals of νCH, amide I and amide II, Figure 6d, most probably for a gold application on the fluorescent damask decorations, and weak signals of an organic compound in the spectra recorded on nonfluorescing areas. Projecting all these data on the t_1 vs t_4 space generated by the PCA model, all the spectra collected on fluorescent damask decorations are located in the upper part of the diagram (full red stars, Figure 6a) corresponding to the *a secco* application by glue or egg. Conversely, the spectra collected on nonfluorescing areas fall in the area of pure *fresco* (open red stars, Figure 6a), because the weak signals of the organic component are not considered relevant by the model.

Organic Binders in Contemporary Paintings. In the present section, a mid- and near-FTIR study for the noninva-

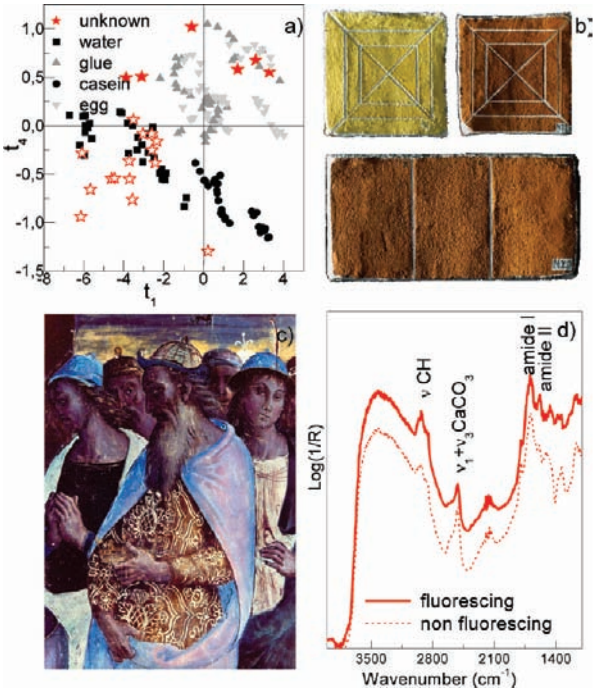

FIGURE 6. Characterization of the organic binders in the wall painting *Adoration of the Magi* by Perugino (1521). (a) t_1 vs t_4 score plot resulting from the PCA calculated on a matrix data set of 150 spectra of replicas painted with water (black square), glue (gray triangle), casein (black circle), and egg (light gray inverted triangle). (b) Images of the replicas. (c) UV-fluorescence imaging of a detail of the painting. (d) Comparison of reflectance mid-FTIR spectra collected on fluorescing and nonfluorescing areas of the Wise King's dress. The stars in (a) refer to the projection of spectral data from fluorescing (full stars) and not fluorescing (open stars) areas of the Wise King's dress.

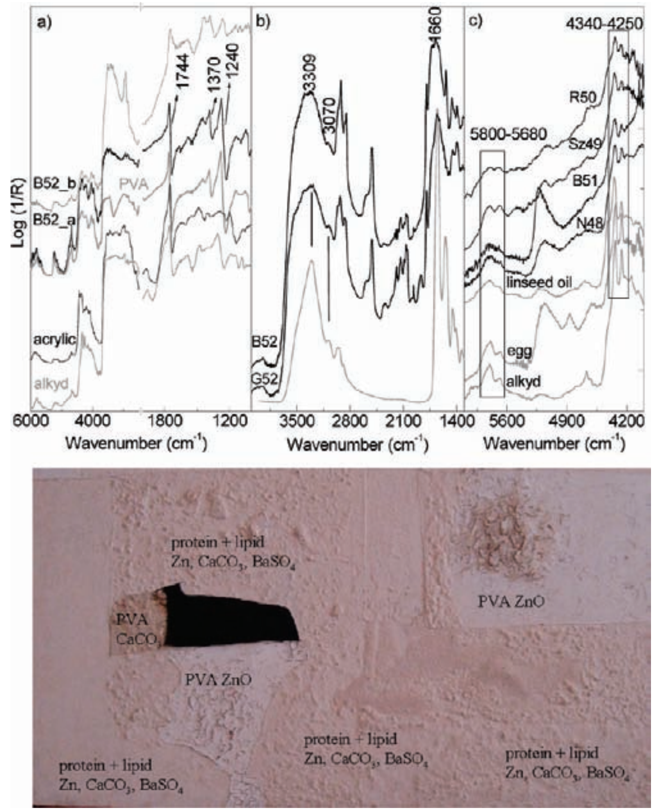

FIGURE 7. Study of Burri's painting technique. Upper: (a) mid-FTIR spectra collected on smooth (B52_a) and rough (B52_b) areas of *Bianco*; for comparative purposes the spectra of standards are reported (gray lines). (b) Mid-FTIR spectra collected on *Bianco* (B52) and *Gobbo* (G52) compared with a glue standard (light gray line). (c) Reflectance near-FTIR spectra acquired on *Rosso* (R50), *SZ1* (Sz49), *Bianco* (B51), and *Nero 1* (N48) compared with the near-FTIR spectra of standards. Lower: Detail of *Bianco*; the compositional distribution is detailed.[27]

sive characterization of organic binders on 18 paintings by Alberto Burri dating from 1948 to 1975 and belonging to the Collezione Albizzini (Città di Castello, Italy) is detailed.[27]

The survey highlighted that Burri widely used poly(vinyl acetate) (PVA) starting from the early works dated to 1948, along with more traditional media such as proteins and lipids. In Figure 7a, two spectra collected on a smooth (B52_a) and rough (B52_b) area of the painting *Bianco* (1952) are reported and compared with the spectra of vinyl, alkyl, and acrylic resins. The combined presence of the ν_{sym}(C−O−C) (at 1240 cm^{-1}) with the intense peak of δ_{sym}(CH$_3$) (at 1370 cm^{-1}) and the weaker signal at 1440 cm^{-1} has been used for the identification of PVA. In the near-infrared region, the $\nu+\delta$(CH) combination bands and the ν(CH) first overtone result in a characteristic profile, distinct for each synthetic resin, thus confirming the presence of PVA. In Figure 7b, two mid-FTIR spectra collected on two paintings are compared with an animal glue standard. The combined presence of signals at 1660 cm^{-1} (amide I), 3070 cm^{-1} (2δNH), and 3309 cm^{-1} (νNH) suggests the presence of a proteinaceous binder. Near-FTIR measurements (Figure 7c) have also revealed the presence of lipidic components, detected by the characteristic doublet at 4340−4250 cm^{-1} ascribed to the $\nu+\delta$(CH) of aliphatic chains and the first overtone of ν(CH) at about 5800−5680 cm^{-1}.[41] Burri employed synthetic and natural binders to obtain different morphologies and optical effects as observed in the white monochrome painting *Bianco* (1952) shown in Figure 7. A multivariate statistical approach applied to the combined vibrational mid-FTIR and elemental XRF data has permitted chemical composition of the white monochrome surface to be mapped, thus correlating the visual morphological differences to specific materials and techniques. Specifically, the multivariate analysis revealed that the "cold" white areas were painted with ZnO mixed with PVA, while the opaque and "warm" white areas with CaCO$_3$, BaSO$_4$, and a minor amount of ZnO mixed with proteins and lipids (Figure 7d). Notably, in

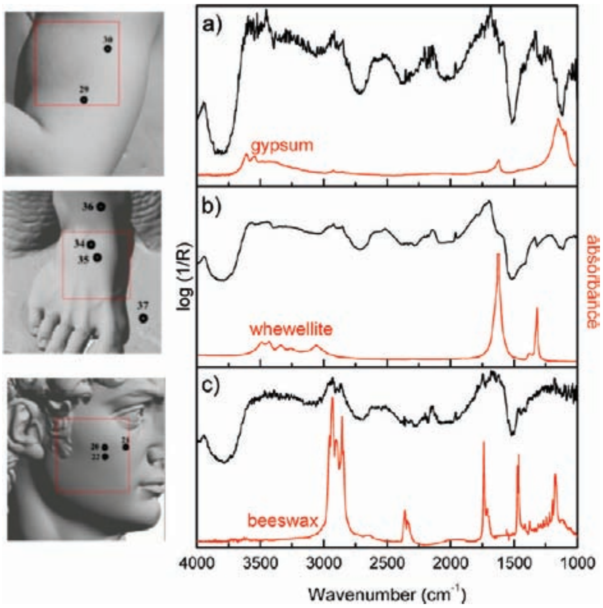

FIGURE 8. Mapping of the surface of Michelangelo's *David*.[21] Reflectance mid-FTIR spectra collected from (a) a sulfate incrustation (on the left arm), (b) an oxalate patina (on the right foot), and (c) a wax contamination (on the right thigh). For comparative purposes, the spectra of standards gypsum, wewhellite, and beeswax are reported in red.

correspondence of the "warm" white areas, Zn carboxylates have also been recognized, likely originating from the interaction of free fatty acids of the lipidic binding medium with zinc oxide.[27]

3.3. Molecular Mapping of Alterations and Contaminants. The value and benefit of applying on-site noninvasive methodologies is not only limited to the characterization of the constituent original materials of a work of art but may also be extended to identifying alteration products and contaminants as well as to monitor online the efficacy and harmfulness of cleaning treatments aimed to their removal. In this context, the MOLAB facility has been successfully exploited to monitor the conservation state and cleaning methods of ancient paintings (by Antonello da Messina and Raphael), modern artworks (by Zolla[42] and Munch), and carbonate sculptures (by Antelami and Michelangelo[21]). In particular, Michelangelo's *David* was studied by portable mid-FTIR spectroscopy within a wide diagnostic program aimed at designing a preventive conservation plan. On-site infrared point measurements, carried out on scaffoldings, allowed for a noninvasive examination of the *David's* entire surface[21] (Figure 8). Sulfates were clearly detected on residual gray incrustations but also in areas that did not appear macroscopically altered, and these were attributed to dry indoor depositions. Oxalates were also identified mainly localized in the lower part of the statue probably due to rain that could have affected the higher part of the sculpture when in its original open air location, leading to the enriched formation of oxalates in the lower part. Spectral features of beeswax have been recognized on specific areas of the sculpture, likely a residue of the detachment additives used during the casting of the *David* in 1847 or from an old protective substance.[21]

4. Breakdowns and Perspectives

The results outlined in this Account demonstrate that noninvasive on-site methodologies have opened up a new way for conservation scientists to analyze artworks giving valuable information for their understanding and long-term preservation, while fully respecting their aesthetical and historical value.

The MOLAB multitechnique approach allows one to overcome the intrinsic limitation of each single spectroscopic method, thus gaining a high selectivity in the identification of materials. Studying easel paintings, the current main limitation concerns the pigments composed of oxides or sulfides of heavy metals (such as lead oxides, arseniate, antimonate and stannate yellows, etc.) that generally are not analyzable by Raman spectroscopy due to the large interference from binder and varnish fluorescence. The recent development of portable equipment for noninvasive X-ray diffraction measurements is opening up the possibility of overcoming these shortcomings.[43,44]

The characterization of organic binders is intrinsically more challenging. However, employing mid- and near-infrared spectroscopy, encouraging results have been achieved, especially in contemporary canvas paintings that are generally less affected by constraints due to the small quantity of organic binder (with respect to wall paintings) or to the interferences from added restoration materials (with respect to ancient paintings). Possible improvements could arise from the combined exploitation of other techniques such as time-resolved fluorescence spectroscopy[45] and unilateral NMR.[46,47] Finally, it is worth underlining that the currently available portable noninvasive methods have strong limitations in fully resolving complex layer stratigraphy. In this regard, it is of interest to mention that the recent efforts to bring the three-dimensional micro-XRF from the synchrotron to the laboratory[48] are paving the way for on-site measurements of three-dimensionally resolved X-ray fluorescence of painting layers.

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