Resumo

A fragilidade e pequeno tamanho das iluminuras torna difícil a aplicação de métodos químicos que requeiram pequenas amostras como é comum fazer em quadros. Em alternativa, técnicas com boa resolução espacial e passíveis de aplicação in situ, como a fluorescência de raios-X dispersiva de energias (XRF) e microscopia Raman têm sido utilizadas para a identificação de pigmentos. Ainda que o número de técnicas não-invasivas esteja a crescer, são todas de aplicação pontual e como tal não são utilizadas para investigar a obra de arte por inteiro. Recentemente descobrimos que combinando os dados obtidos através de técnicas de imagiografia multiespectrais, baseadas em reflectância de VIS-NIR e luminescência, com métodos pontuais como a espectroscopia de UV-VIS por reflectância com fibra óptica (FORS) e XFR, é possível identificar e mapear os pigmentos principais utilizados em iluminuras bem como visualizar o desenho preparatório e eventuais alterações na composição. Descrevem-se exemplos do procedimento experimental e dos resultados obtidos em diversos fólios iluminados. ●

palavras-chave

IMAGIOGRAFIA MULTIESPECTRAL
FLUORESCÊNCIA DE RAIOS-X
DISPERSIVA DE ENERGIAS
FORS
ILUMINURAS

Abstract

The fragility and small dimensions of illuminated manuscripts prohibit the use of chemical methods that rely on small samples being taken from the artwork as is typically done for paintings. Instead site-specific in situ *techniques such as X-ray fluorescence (XRF) and Raman spectroscopy are commonly used to identify pigments. While the number of non-invasive analytical techniques is growing, all are site-specific and thus cannot be used to survey the entire work of art. Recently we have found that by combining results from multispectral visible/infrared reflectance and luminescence imaging spectroscopy with those from site-specific methods such as fiber optics reflectance spectroscopy (FORS) and XRF, it is possible to successfully identify and map the primary pigments on medieval illuminated leaves, as well as visualize the underlying preparatory sketches and compositional changes. Examples of the experimental workflow and results obtained by using it to study several illuminated leaves are presented. ●*

key-words

MULTISPECTRAL IMAGING
X-RAY FLUORESCENCE
FORS
MANUSCRIPT ILLUMINATIONS

COMBINING VISIBLE AND INFRARED IMAGING SPECTROSCOPY WITH SITE SPECIFIC, *IN-SITU* TECHNIQUES FOR MATERIAL IDENTIFICATION AND MAPPING

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Introduction

The work being carried out at the National Gallery of Art, Washington DC (NGA), is aimed at adapting the imaging spectroscopy methods, originally developed for remote sensing, for use in conservation science, and in particular to explore the resulting synergy when these results are combined with *in situ* chemical methods. Of particular interest is the study of illuminated manuscripts, which have a simpler palette than many paintings and often cannot be sampled.

Among the many questions often addressed in the analysis of illuminated manuscripts, two are most relevant for conservation science. Namely, the identification of the materials used, particularly the colorants, and elucidating the construction techniques used such as layering and the use of preparatory sketches. Site-specific analytical techniques, such as X-ray fluorescence (XRF) and Raman spectroscopy,

are usually employed to identify the pigments and possibly the binders used for the illumination. While such methods are analytically powerful, they cannot be used to survey the entire surface of a miniature. With both techniques, spectra are usually acquired on visually identified sites thought to be representative of the pigments and mixtures used for the illumination. Such visual inspection may not always ensure an adequate representation of the pigment diversity present.

On the other hand visual imaging techniques such as microscopic observation, infrared reflectography (IRR), and UV-excited fluorescence, are employed to visualize the preparatory sketches and understand the layer structure of the miniature. Radiometric calibration of images acquired in numerous visible/infrared spectral bands can be used to produce quantitative results, thus «transforming» the imaging process into «imaging spectroscopy», which can provide chemical information about materials. This is done by generating reflectance and luminescence spectra at each pixel and thus over the whole imaged art object. In recent years, research carried out mostly on paintings has proved that imaging spectroscopy techniques can be effectively used for material identification and mapping on works of art (Casini et al. 1999, Delaney et al. 2005, Delaney et al. 2009a, Delaney et al. 2010). However such imaging spectroscopy methods have required light levels too high for works of art on paper or parchment. Here we present some results regarding the use of a high sensitivity multispectral visible/infrared camera system (400 to 2500 nm, 15 spectral bands), which operates at illumination levels of approximately 150 lux. We have used this camera system to acquire reflectance and luminescence images of several 14th century Italian illuminated leaves in the NGA collection, notably, one attributed to the workshop of Pacino di Buonaguida, representing «Christ in majesty with twelve apostles», and another attributed to Niccolò da Bologna, representing the «Birth of John the Baptist». Combining the imaging spectroscopy results with data from low light fiber optics reflectance spectroscopy (FORS) and X-ray fluorescence, we have found that the primary pigments on these medieval illuminated leaves can be identified and mapped, and preparatory sketches and changes can be visualized (Delaney et al. 2009c, Ricciardi et al. 2009).

Summary of experimental techniques

Imaging spectroscopy involves the acquisition of spatially co-registered images in many spectral bands in order to allow construction of a spectrum at each point in the spectral image set (Fig. 1). In the case of *reflectance imaging spectroscopy* the spectral features collected relate to the electronic transitions and some vibrational modes of the artist's materials. By grouping similar spectra maps can be made, and the average spectra from each map can be compared to data-bases to help with the identification. *Luminescence imaging spectroscopy* exploits the observation that a subset of artists' pigments, mostly organics dyes, is luminescent when excited with UV/blue light. This is useful to help in the identification of pigments which have
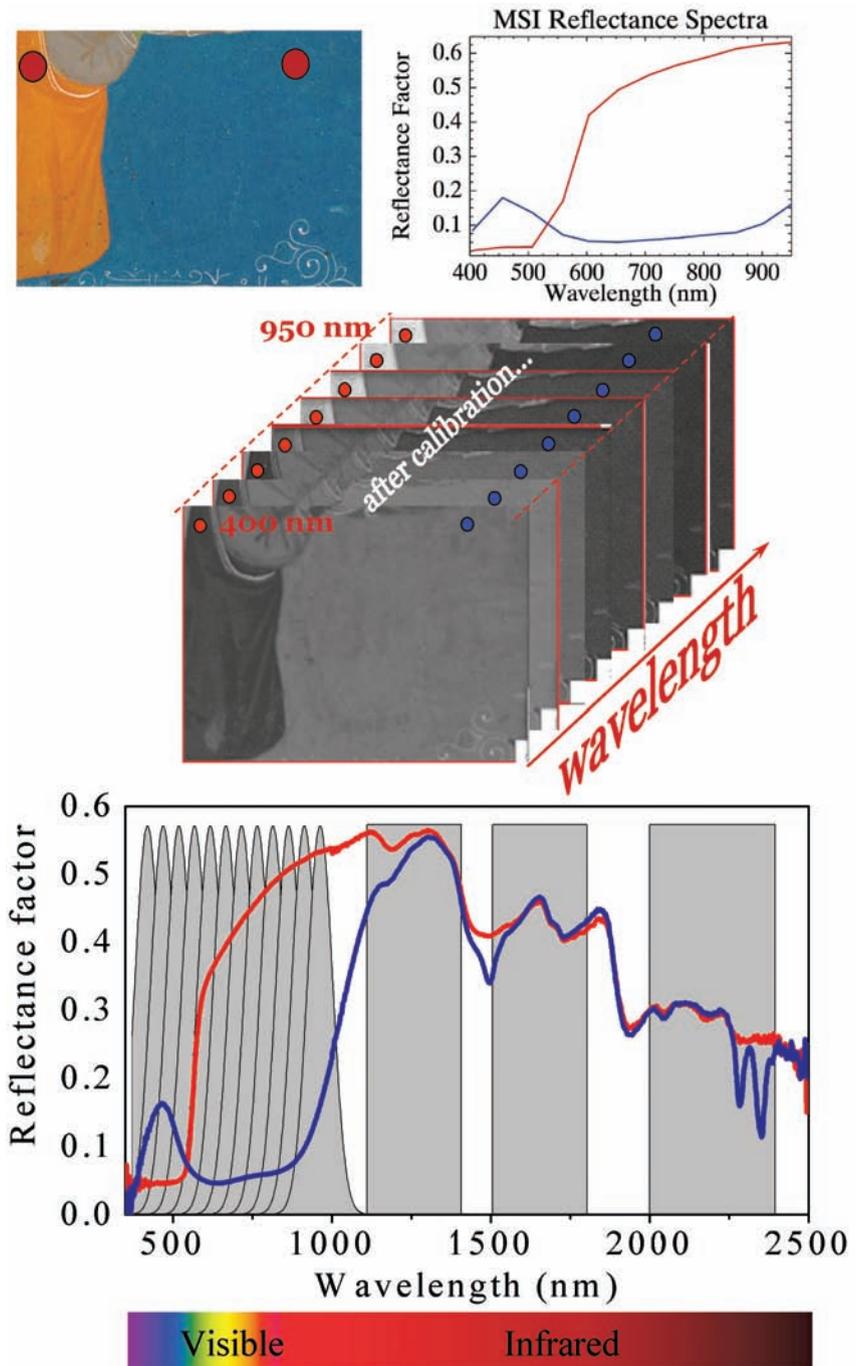
FIG.1 (TOP) SCHEMATIC REPRESENTATION OF THE WORKING PRINCIPLE OF REFLECTANCE IMAGING SPECTROSCOPY, WITH THE RECONSTRUCTION OF THE REFLECTANCE SPECTRA FOR A BLUE AND A RED AREA FROM THE MULTI-SPECTRAL IMAGES OF «CHRIST IN MAJESTY WITH TWELVE APOSTLES» BY THE WORKSHOP OF PACINO DI BUONAGUIDA (VISIBLE IMAGE DETAIL AT TOP LEFT); (BOTTOM) HIGH-RESOLUTION REFLECTANCE SPECTRA OF THE SAME AREAS COLLECTED WITH THE FIBER OPTICS REFLECTANCE SPECTROMETER. THE GRAY GAUSSIANS AND RECTANGLES REPRESENT THE WAVELENGTH RANGES ANALYZED BY THE IMAGING CAMERAS

reflectance spectra that lack unique features, as may be the case for organic dyes, and it is for this reason that it is useful for the analysis of illuminated manuscripts. As noted before, the use of imaging spectroscopy for the study of light-sensitive materials such as illuminated manuscripts can be problematic; to date in fact, many of the multi-spectral imaging (MSI) camera systems having high spatial fidelity require high light levels. The study of works of art on paper and parchment requiring low illumination (about 150 lux, comparable to a few times gallery light levels) is currently carried out at NGA with an optimized low-noise, high-sensitivity 4 mega pixel Si-CCD imaging camera. This system is used to collect 12 narrow-band reflectance and luminescence images in the visible to near infrared range (400 to 950 nm, 40 nm FWHM). While multispectral imaging spectroscopy in this spectral range (visible to near infrared) is a powerful tool to spectrally separate and cluster similar materials it is not robust enough to identify directly most artist's materials. Thus site-specific methods such as XRF and FORS can be used to aid in the identification.

Infrared reflectograms (IRR) in the 750 to 950 nm and 1000 to 2500 nm range can be acquired using the Si-CCD camera (see above) and a highly sensitive InSb camera equipped with infrared filters, allowing the observation of preparatory sketches and compositional changes at the same low light level used for MSI. IRR is also useful to distinguish between the materials used for underdrawings; most iron-based inks are in fact totally transparent in the 1000-2500 nm range, while carbon-based inks and most metalpoints remain visible throughout this range.

Fiber Optics Reflectance Spectroscopy (FORS) is used to collect higher resolution reflectance spectra in selected areas in the 350 to 2500 nm range, allowing access to the short-wave infrared region, which yields important information for the identification of certain materials such as azurite (easily recognizable by two absorption bands at about 2285 and 2352 nm), lead white, and gypsum. Derivative spectra can be used to distinguish for example between red lead and vermillion, thanks to the difference in the position of the transition edge (~570 vs. ~595 nm, respectively). The interpretation of spectra acquired on mixtures is, however, not always straightforward. The presence of numerous parchment-related absorption bands in the infrared range also makes it harder to separate which spectral features actually relate to the pigment. In both cases, additional data treatment is required.

X-ray fluorescence (XRF) analyses are carried out using a Bruker ARTAX Pro instrument equipped with a Rh tube and 75 µm capillary optics. A helium flush is used to be able to detect light elements ($> Na$). Whenever possible, areas for analysis are chosen so that no decoration is present in the corresponding area on the verso of the manuscript leaf, in order to avoid confusing results due to the intrinsic limitation of XRF which does not yield results spatially resolved in depth. It is worth noting that XRF analyses of works of art on parchment are difficult due to the low density of this material, which creates a large amount of inelastic scattering in the spectrum compared with the small amounts of material actually being analyzed in the manuscript. XRF data are interpreted using traditional methods, i.e. the combination of elements identified in each spectrum is compared with possible pigment/mixture

compositions. This leads to several possible assignments and thus not always to a unique answer. Comparing these results with those from the spectral methods can help finalize the assignment to the most likely candidate.

Methodology

First, the multispectral reflectance image cube is constructed from 12 reflectance images (400 to 950 nm). Second, the luminescence image cube (500 to 900 nm) is constructed from images acquired while the manuscript is illuminated with blue light (380 to 450 nm) to excite the fluorescence. Next, infrared reflectance images are collected in three spectral bands: 1100 to 1400 nm, 1500 to 1800 nm and 2000 to 2400 nm, and added to the multispectral reflectance cube. The reflectance and luminescence images are processed to correct for pixel and illumination non-uniformity and calibrated to reflectance or emittance using standards. These calibrated images are then spatially «registered», i.e. aligned together to remove lens and filter related image shifts. Spatial maps of the primary spectral elements can be made directly by probing the low-resolution reflectance image cube with a reference spectrum. The reference spectrum can come from a spectral library, from a user selected site in the image cube, or as result of principle component based analysis with software designed to find the primary spectral components. The cube is probed with the spectral angle mapper algorithm which finds pixels having similar spectra to the reference spectrum. These maps are produced using all 12 spectral bands as opposed to creating false color maps from just three bands, ensuring more meaningful results. In a similar manner the luminescence spectral cube can be probed and maps of areas having the same emission spectra found. These maps then can be used to guide selection of sites where more definitive *in situ* analysis can be performed, such as XRF, Raman spectroscopy, or fiber optics reflectance and luminescence spectroscopy. An example of the experimental workflow used during the study of the «Christ in majesty with twelve apostles» by the workshop of Pacino di Buonaguida, is illustrated in Fig. 2. It should be noted that imaging in the 400-1600 nm range can be easily performed with relatively inexpensive equipment, quite commonly found in Conservation Departments.

Case Studies

In the case of the illuminated manuscript leaves analyzed at NGA, the described analytical methodology yielded distribution maps for several pigments typically used for illuminations in the Middle Ages (Brunello 1975), i.e. regions of azurite, ultramarine, vermillion, and brown earth, along with some indication of pigment layering in the blue and red areas. In two separate cases (Delaney et al. 2009b, Ricciardi et al. 2009), the use of imaging spectroscopy allowed, among other things, to map selected blue

FIG.2 EXPERIMENTAL WORKFLOW USED TO COLLECT AND ANALYZE THE REFLECTANCE IMAGES FOLLOWED BY SITE-SPECIFIC ANALYSIS, AS CARRIED OUT DURING THE STUDY OF «CHRIST IN MAJESTY WITH TWELVE APOSTLES» BY THE WORKSHOP OF PACINO DI BUONAGUIDA (ROSENWALD COLLECTION, ACCESSION NUMBER 1952.8.277, IMAGE COURTESY OF THE NATIONAL GALLERY OF ART, WASHINGTON DC)

areas not identified by other techniques, where a layer of ultramarine was painted over azurite, a practice which was common in 14th century Italy (Bomford et al. 1989). XRF and FORS analyses of selected sites, chosen following the indications provided by the MSI maps, specifically showed the presence of lead white and «mosaic gold» (tin sulphide). The presence of organic dyes was identified and mapped through the analysis of the luminescence image cubes. The reflectance and luminescence datacubes therefore allowed mapping the pigment distribution and layering on the illuminated leaves in a totally non-invasive and relatively fast way, not requiring a time-consuming detailed observation under the microscope. They also helped «guide» the choice of the sites to be analyzed by XRF and FORS for more accurate pigment identification.

During the analysis of «Birth of John the Baptist» by Niccolò da Bologna (Ricciardi et al. 2009), infrared reflectograms revealed a few preliminary sketches, either executed with a carbon-based ink on a fine brush, or with a metalpoint. The near infrared images also showed that the skin tones were loosely painted and do not always match the finely detailed preparatory lines.

Additional remarks

In order to produce results which are relevant from the point of view of art histori-cal issues, scientific analyses are usually applied to many, if not all, the illuminated manuscript leaves contained in one manuscript. The final goal is a comprehensive characterization of the manuscript, obtained by the identification and mapping of the primary pigments, and by the observation of preparatory sketches. The availabil-ity of a relatively quick procedure would allow surveying a large number of leaves, increasing the possibility to obtain significant results and providing a chance for extensive comparisons. The analysis of each miniature, including data acquisition and treatment, following the methodology presented in the previous sections, at the moment requires two days for the MSI and IRR, at least one day each for XRF and FORS. Significant, if preliminary, results on a single illuminated manuscript leaf can thus be obtained in about a week. This is therefore a «quick» and effective methodology compared to the time (and effort) which would be required to obtain pigment identification and mapping at a comparable level using only site-specific methods, such as Raman spectroscopy and XRF, which would have to be performed on hundreds of spots.
In the future starting with the MSI-derived maps improved results could be obtained by combining XRF, FORS, and Raman spectroscopy into a single setup, which would allow acquiring different kinds of information on the same sites, yielding a complete characterization of the materials in situ (e.g. identification of the binding media and organic pigments).

Conclusions

The combination of reflectance and luminescence imaging spectroscopy, FORS, and XRF has proved useful for the identification and mapping of the primary pigments on medieval illuminated manuscript leaves. Imaging spectroscopy, even in only a few bands, has shown its utility for pigment mapping; the imaging was made «quantita-tive» thanks to calibration and this allowed reconstructing reflectance and emission spectra. This approach of combining high fidelity site-specific methods (FORS and XRF) with the mapping capability of multispectral reflectance and luminescence imaging spectroscopy appears thus to be a useful tool, providing improved in situ mapping and identification of pigments on illuminated manuscripts in a relatively short time. This methodology can be further refined, for example by improving the correlation between the luminescence and reflectance images in order to improve the characterization of organic dyes and yellow pigments. Finally, the identification of the organic binding media could be attained by adding Raman spectroscopy or mid-IR spectroscopy to the list of analytical techniques. ●

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