Multispectral and hyperspectral imaging technologies in conservation: current research and potential applications

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Abstract

Spectral imaging technology, which records simultaneously spectral and spatial information about an object, was initially developed for remote sensing and has since been successfully applied to other areas of research. Although relatively new to the field of conservation, this non-invasive method of investigation has already provided promising results in the analysis of paintings and written documents, the characterization of materials and digital documentation. This article reviews the published literature relating to the application of multispectral and hyperspectral imaging for the study and conservation of works of art and presents some new perspectives offered by this innovative and fast-developing technology.

Introduction

Spectral imaging technology was developed some 40 years ago and until the early 1990s its use was mainly restricted to astrophysics, remote sensing and terrestrial military applications [1]. Originally described as 'multispectral' imaging, the continuous increase in the number of spectral bands resolved by successive generations of imaging spectrometers has led to the appearance of the term 'hyperspectral'. Indeed, this technology has undergone a rapid development during the last 20 years, largely driven by the evolution of semi-conductors and related detector focal plane arrays. While most of the research efforts are still focused on remote sensing applications [2, 3] technical advancements have led to the emergence of this technology in other fields of research, including medicine, pharmacology, environmental sciences, food engineering, agriculture and the management of natural resources [4–8].

Over the last decade, spectral imaging has also gained importance in the field of conservation. Building upon the extensive application of infrared reflectography (IRR) in the study of paintings, spectral imaging has significantly enlarged the possibilities of IRR, first with the use of broadband filters [9–11] and later with the introduction of narrowband filters [12, 13]. This non-invasive method of investigation, which allows the simultaneous collection of spectral and spatial information, thus extending the capabilities for diagnostic imaging, has proven to be a useful technique for both conservation scientists and conservators. Primarily used for scientific investigations of paintings, it has also been successfully applied to the study of documents, the evaluation of conservation treatments and digital imaging for documentation.

This paper presents an overview of current research and potential applications of spectral imaging in the study and conservation of works of art. The principles of spectral imaging are introduced, together with a description of available instrumentation. Papers published during the last 10 years are reviewed and different issues related to instrumentation, data collection and post-processing methods are addressed. The advantages and limitations of spectral imaging technology are discussed in the context of the specific needs and requirements of conservation applications. New perspectives on the application of this technology to the field of conservation are presented, based on results obtained in other domains and on recent developments in infrared detector technologies. Finally, directions for further research are suggested in order to support these new potential applications.

Principles and instrumentation

The fundamentals of spectral imaging are based primarily on the interaction of light with matter. Light and other electromagnetic radiations are commonly described in terms of their wavelengths, but the designation of spectral ranges varies often with the application, especially for the infrared [14, 15]. To be consistent with the papers described in this review, the following nomenclature will be used – visible (VIS): 0.4–0.7 µm; near-infrared (NIR): 0.7–1.0 µm; short-wave infrared (SWIR): 1.0–2.5 µm; and mid-infrared (MWIR): 2.5–15 µm. The near-infrared range is sometimes grouped with the visible and referred to as visible-near-infrared (VNIR).

When a photon is incident on a surface of a medium, energy can be absorbed, transmitted and/or reflected by that surface, with a wavelength dependency determined by the material properties. The ratio of the energy reflected or scattered by the surface to the incident energy is termed the reflectance. The spectral reflectance is the reflectance per unit wavelength and transforms into a spectral reflectance curve when measured over a given spectral range. Spectral reflectance depends not only on the scattering properties of the material under investigation, but also on the characteristics of the illumination and viewing geometry and the sensitivity of the detector. The theory of scattering processes applied to material surfaces and particulate media has been extensively researched and is beyond the scope of this review; for more details see [16, 17].

For a particular surface or object, the reflectance spectrum shows characteristic bands induced by electronic and vibrational absorption processes of the constituent materials. Spectral reflectance therefore provides essential information about material properties, such as color and composition. Reflectance spectroscopy, especially in the VNIR and SWIR spectral ranges, was first used in the identification of minerals, so geological applications have been the principal driving force behind much of the early

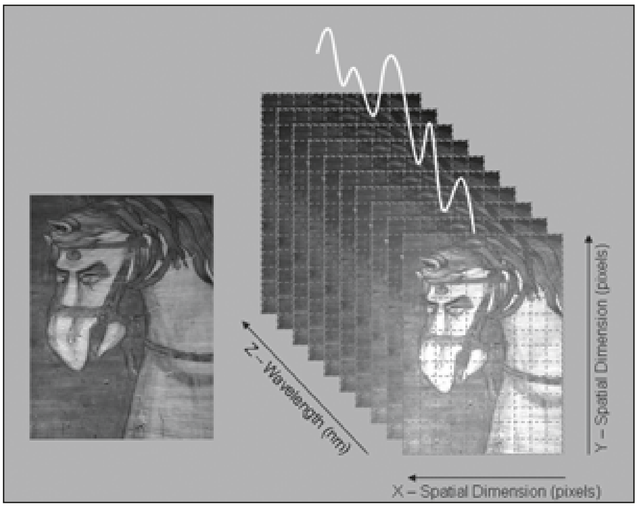

Fig. 1 Schematic representation of a multispectral image cube displaying both spectral and spatial information

development phases of spectral imaging in remote sensing [18, 19].

During the last decade, spectral imaging has been increasingly used for field and laboratory applications. Whether operated from a satellite, an aircraft, in the field or in the laboratory, the final objective of spectral imaging remains the same: to provide spatially-resolved analysis and distribution maps of materials with distinct spectral signatures. Spectral imaging systems used in conservation are capable of acquiring and analysing high definition images across multiple spectral bands of broad or narrow band width. Depending on the spectral resolution, it may be possible to calculate a full spectrum per image pixel from the acquired spectral cube that contains both spectral and spatial data (Figure 1). These systems are basically composed of a filtering or dispersing device and a camera/detector interfaced to a computer. Dedicated software is used to operate the system and to control image and data acquisition.

Detectors

Different detector technologies have been developed to capture images in the ultraviolet, visible and infrared parts of the electromagnetic spectrum [20, 21]. The most common detectors in the visible range are charge coupled device (CCD) focal plane arrays (FPA) made of silicon with cut-off wavelengths of around one micron. The majority of standard CCDs display low quantum efficiency in the blue and ultraviolet regions because of the high absorption coefficient of silicon in these spectral regions. Better performances are achieved with thinned back-illuminated and cooled CCD detectors, albeit at an additional cost [21, 22]. For the wavelengths in the ultraviolet range, high quantum efficiency detectors made of aluminum gallium nitride are also available in arrays up to 320 × 256 pixels [23].

Low-cost lead oxide-lead sulfide (PbO-PbS) vidicons have been routinely used for the visible-SWIR range despite their low sensitivity and resolution compared with recently-developed solid state FPAs [24]. Infrared FPAs cover different spectral ranges between 1 µm and 25 µm and are based on various materials, including platinum silicide (PtSi), indium antimonide (InSb), indium gallium arsenide (InGaAs) and mercury cadmium telluride (HgCdTe or MCT) [25, 26]. PtSi detectors have been widely used and are affordable because of their compatibility with silicon technology. However, their quantum efficiency is rather low and as (or like) InSb detectors, sensitive in the 1–5 µm spectral range, they must be cooled down to around 80°K [20].

InGaAs and MCT detectors were originally developed for high-end technologies and military applications. Since their declassification their use for commercial applications has grown steadily, supported mainly by rapid progress in opto-electronics and materials science [27]. Standard InGaAs detectors ($In_{0.53}Ga_{0.47}As$) grown on indium phosfide (InP) substrates are sensitive in the 0.85–1.7 µm spectral range and currently available in formats up to 640 × 512 pixels [28]. Better performances might be achieved by growing the InGaAs on a gallium arsenide (GaAs) substrate [29, 30].

MCT detectors cover almost the entire infrared region (1–20 µm) and their spectral cut-off can be finely tuned over the whole spectral range by varying the Hg:Cd ratio in the composition of the semi-conductor [27, 31]. For applications above 3 µm, MCT detectors need to be cooled down to liquid nitrogen temperatures, but SWIR–MCT detectors can operate at around 200° K with Peltier cooling. The materials and process technologies used in their manufacture mean that MCT detectors are the most expensive kind available, and commercial SWIR–MCT cameras are only available with a 320 × 256 pixel array [32]. Recently, new processing methods have also led to the development of standard InGaAs and SWIR–MCT detectors sensitive in the visible light range, allowing coverage of the 0.4–1.7/2.5 µm spectral range with one single array [33, 34]. However, the quantum efficiency of these detectors in the visible light range is much lower than that of CCDs.

Filtering and dispersing devices

Different categories of devices are used to separate or filter wavelengths, each presenting advantages and disadvantages. Their integration in a specific system often depends on the final application. Commonly used devices are based on optical filters, prism-grating-prisms (PGP) and electronically tuneable elements such as liquid crystal (LCTF) and acousto-optic (AOTF) tuneable filters [35].

Among the systems using optical filters, effective separation may be achieved with mechanical scanning devices using broadband and/or narrowband interference filters placed on a rotating wheel in front of the detector to filter the incoming radiation. However, mechanical scanning devices have some disadvantages: they hold only a limited number of filters and the rotation of the filter wheel for the filter-changing process often causes vibrations that could result in image registration problems [22]. Moreover, the tuning speed is relatively slow and they are often not truly portable, although compact designs based on this technology and equipped with a relatively large number of filters have been intelligently integrated in spectral imaging systems [36].

LCTF [22, 27] and AOTF [22, 37] operate on different principles, but both share similar advantages: they contain no moving parts and they have high tuning speeds and compact design [38, 39]. LCTF and AOTF can be electronically tuned in a stepwise or random mode from the visible through the mid-infrared, but different modules are necessary to cover a large spectral range. LCTFs have a low response in the blue light region that can be partially mitigated through longer exposure times [40]. AOTFs have a tuneable response that is independent of wavelength, but might produce some image shifting [41]. The high tuning speeds are of the order of milliseconds for an LCTF, going as high as microseconds for an AOTF.

PGP dispersing devices use transmission holographic gratings with high diffraction efficiency of up to several hundred bands, offering real hyperspectral capabilities [42]. While spectral imaging systems equipped with optical filters and electronically tuneable filters record the two spatial dimensions and temporally sample the spectral dimension, a PGP records the spectral and one spatial dimension while temporally sampling the second spatial dimension. For immobile targets, PGP devices need to scan the entire object to collect data before an image can be generated, which prevents real-time imaging. Although not very common, spectral imaging systems equipped with a PGP have been used in conservation for the study of paintings and other materials [43–45].

Multispectral (MSI) and hyperspectral (HSI) imaging systems

Over the last two decades, different detector and filtering/dispersing technologies have been integrated in custom-made or commercial spectral imaging systems [46–49]. The main characteristics of the systems used in the field of conservation are summarized in Table 1 with the applications for which they have been used. Most of them, however, offer enough flexibility to be used successfully for other applications as well.

Table 1 Characteristics of multispectral and hyperspectral imaging systems used in conservation

References	*Detectors*	*Spectral range (nm)*	*Dispersing device / number of filters or bands*	*Applications*
50	Vidicon PbO-PbS	400–1000	Broadband filters	Paintings
12 51	CCD Vidicon PbO-PbS PtSi Ge	400–2500	Optical filters	IR reflectography
24, 52	Vidicon PbO-PbS	400–1600	Optical filters / 29	Paintings, pigments
53, 54	CCD	400–1000	Optical filters / 62, 14 LCTF / 15–20 bands	Rock art, pigments, inscriptions
43	CCD	400–1700	PGP / 256 bands	Semi-precious stones
55–57	CCD	650–1040	LCTF / 40 bands	Paintings, pigments
36, 58–60	CCD	380–1000	Optical filters / 33	Paintings, palimpsests, manuscripts, marble
61, 62	CCD	400–700	LCTF / 31 bands	Paintings, colour reproduction, metamerism
63	CCD Vidicon PbO-PbS InGaAs HgCdTe	800–2500	Cut-off filters	IR reflectography
64	CCD	400–700	Broadband filters	Gems, metamerism
65	CCD PtSi	450–1600	Optical filters / 8 VNIR, 3 SWIR	Paintings, pigments
66	Vidicon PbO-PbS	400–2200	Optical filters / 29	Drawings
67, 68	CCD	400–700 450–1000	Broadband filters / 7 Broadband filters / 12	Paintings (conservation, documentation, archiving)
69, 70	CCD	400–1000	Broadband filters / 13	Paintings (conservation, documentation, archiving)
71	CCD	400–1000	Interference filters / 13	Paintings, pigment identification
72	CCD	400–1000	Optical filters / 5	Paintings
73	CCD	400–700	LCTF / 31 bands	Paintings, documentation
74	CCD	380–1100	Tuneable light source	Documents, inks

Data processing

One important aspect of spectral imaging is that it generates a large amount of data, which may be difficult to handle, view and interpret [75]. The size of a spectral image cube can easily reach several tens of megabytes and post-processing methods are needed in order to fully exploit the information contained in the image cube. The main goal of multispectral data processing is to distinguish and identify materials from their spectral signatures and to spatially group pixels with similar characteristics [76]. A variety of methods with various tradeoffs in flexibility, accuracy and speed are available to perform this task. It is beyond the scope of this paper to describe these methods in detail, but they are primarily based on spectral transform and multivariate statistic techniques such as spectral angle mapping, principal component analysis (PCA), linear discriminant analysis (LDA), fuzzy C-means (FCM) and neural networks [55, 77–81]. PCA has been widely used for conservation applications, either as a stand-alone technique [52, 57, 66, 82] or to reduce the dimensionality of datasets prior to another classification algorithm [43].

Current applications in conservation

The application of spectral imaging technology in conservation is still at an early stage. However, its potential has already been witnessed through studies in which paintings have been attributed and interpreted, pigments and inks differentiated and identified, and important illegible scripts revealed, enhanced and studied. Color has also been accurately reproduced. Spectral imaging has revolutionized non-invasive techniques such as infrared reflectography, ultraviolet reflectance and ultraviolet induced visible fluorescence, commonly employed for the study and conservation of artifacts.

This section reviews published literature on the application of spectral imaging technologies in art conservation and is discussed under three main categories:

- Study of materials of archaeological, cultural and historic value
- Monitoring and evaluation of conservation treatments
- Digital imaging for documentation and archiving

Although important, research in the characterization of archaeological and artistic materials using other non-invasive imaging methods of examination and analysis, such as fluorescence lifetime imaging, will not be discussed.

Study of materials of archaeological, artistic, cultural and historic value

Visualization of underdrawings and pentimenti in paintings

Infrared reflectography (IRR) has been the technique most widely used for the imaging and study of underdrawings [83]. In his seminal work on the optical properties of thin paint films, Van Asperen de Boer found that maximum penetration of most paints can be achieved at wavelengths of around 2 µm [9]. However, at wavelengths near to 2 µm, the common drawing materials, namely iron gall ink and sepia, become invisible [13]. This suggests that the combined optical properties of a specific paint and underdrawing system determine which spectral bands can be used to effectively visualize the underdrawing [51].

Limitations in the performance of the vidicon camera at around 2 µm and its poor image resolution [13] prompted the search for imaging systems capable of screening a certain spectral range in order to find the wavelength best suited to imaging the underdrawing. Delaney et al. [12] and Walmsley et al. [51] investigated the capabilities of different cameras equipped with broadband filters for the visualization of underdrawings and found that germanium and PtSi detectors were superior to vidicon tubes. Optimal visibility of most underdrawing materials was attained at around 1.8 µm whereas 2 µm and over was necessary for selected pigments. Recently, in a similar approach, Gargano et al. [63] came to the same conclusions regarding the optimal spectral range using cameras integrating the latest detector technologies. They also suggested the usefulness of a CCD camera despite its limited spectral range.

High image resolution and penetration have always been the two most important parameters that conservators have sought in IRR devices. However, as seen above, not all underdrawings are visible in the infrared, and MSI could assist in finding the right wavelengths to image

Figs. 2a and 2b Monochromatic spectral images at 640 nm and 1000 nm of a Byzantine icon showing an increase in the reflectivity of the paint layer at 1000 nm. At this wavelength, the painterly pentimenti of the hand beneath become visible (Kakoulli 2003) underdrawings (Figures 2a and 2b). Moreover, in the study of paintings it is important to image not only the underdrawings but also the under-modelling and colored grounds that could be significant for the attribution of paintings [84]. Optimized imaging systems combined with the analytical capabilities of MSI can therefore provide an invaluable contribution to this field of imaging.

Characterization and mapping of pigments and inks in painted artifacts and drawings

Non-invasive characterization of pigments and other pictorial materials has been primarily performed using fibre optics reflectance spectroscopy (FORS) in the UV-VIS and NIR and more recently in the MWIR [85–91]. The development of MSI systems capable of providing imaging spectroscopy has opened new perspectives for this application. Such systems capture images at a large number of spectral bands and can identify materials with unique spectral signatures. Moreover, with adequate data-processing methods, these materials can be mapped based on their spectral characteristics, which is a significant advantage compared with spectroscopic point analysis. However, the spectral resolution of spectroscopic techniques is still much higher than that of MSI systems and the former are often used to support the processing and interpretation of MSI results [24, 52, 92].

In 1998, Baronti et al. [52] published the results of their examination using MSI technology of the painting *Holy Trinity Predella* by Luca Signorelli, which was displayed at the Uffizi Gallery in Florence. Twenty-nine images were acquired in the VNIR spectral range (see Table 1). The reconstructed spectra were correlated with high-resolution spectra obtained from a bench spectrometer, but showed different values of the offset since backscattered radiation was recorded by the bench spectrometer in addition to the specular radiation. PCA was used to process the images in order to reduce their dimensionality in more meaningful sets and to facilitate their interpretation. In the processed images, materials were identified, regions in the painting with similar spectral signatures were mapped and obscured areas were enhanced.

Mansfield et al. [55] used a similar approach with a LCTF for the characterization of organic and mineral inks in a sixteenth-century drawing at the Winnipeg Art Gallery attributed to the School of Pieter Bruegel the Elder (Table 1). The captured images were analyzed with unsupervised FCM cluster analysis and LDA. FCM did not provide the desired information as almost all spectral variations resulted from differences in the spectral absorbance of the paper (background) itself. The application of LDA, however, revealed areas of the ink or its decomposition products.

Casini et al. [24] used MSI in the 400–1600 nm spectral range for the study of an important painting by Pontormo, *La Strage degli undicimila martiri* from the Pitti Palace collection (Table 1). Based on the spectral differences between two yellow pigments in the painting (goethite and lead-tin yellow), MSI provided spatially resolved analysis and distribution maps within the layer structure of the painting and assisted in the identification of possible overlapping areas of the two pigments. Using a similar system, Bacci et al. [66] investigated a set of drawings on paper by Parmigiano. Although MSI is particularly well adapted for the non-invasive study of such fragile artifacts, they were unable to identify the pictorial materials precisely due to limited spectral resolution. Liang et al. [71] have used an MSI system for the study of the blue, red and green pigments of the painting *St. Mary Magdalene* by the Venetian artist Carlo Crivelli (Table 1). They were able to identify the blue pigment from the robe of St. Mary as azurite and the red pigment from her bright red cloak as cinnabar. The spectrum of the unknown green pigment from the lining of the cloak matched those of verdigris, Scheele's green and emerald green mixed with white, while the spectrum of the red brocade on the sleeve indicates the presence of a lake pigment. Neither the green nor the red pigment (from the brocade of the sleeve) could be unambiguously identified with the current method using the VNIR as in this wavelength range several pigments display similar reflectance spectral characteristics.

VNIR spectral imaging has also found innovative applications for the in situ study of mural paintings and rock art [53, 54, 93]. Despite the constraints imposed by outdoor measurements on large-scale paintings and inscriptions, spectral differences in pigments with similar coloration but different chemical composition were recorded in the Mayan hieroglyphs found at the Naj Tunich cave in Guatemala [53, 54]. The data obtained were further analysed by clustering analysis, which led to differentiation between original pigments and later repainting, and revealed interrelationships between the inscriptions. The study of English medieval wall paintings with MSI has revealed the use of cinnabar through a comparison of the results with reference spectra and data from other analytical techniques, but pigment mixtures could not be identified [94]. The identification of a red pigment as vermilion from an illuminated manuscript was also achieved with MSI, whereas the blue pigment could not be identified due to limitations in the spectral range [36, 95].

MSI in the SWIR spectral range with a limited number of broadband filters (Table 1) has been recently used by Delaney et al. [65] and opens up new possibilities for the characterization of pigments with similar reflectance in the VNIR. Results on test panels show a good correlation with the reflectance spectra obtained by high resolution VNIR-SWIR spectroscopy. The respective images collected as image spectral cubes were also used as a visual criterion to differentiate the pigments, as they showed clear differences at varying wavelengths [65, p. 128]. A parameter that seems to affect the intensity of the spectra is the light-absorbing white ground often found as a preparatory layer beneath thin paint that alters the reflectance spectra of the paint layer. The same methodology for MSI in the SWIR range was also applied in the examination of blue pigments in two works by Van Gogh: *La Mousmé* (1888) and the *Van Gogh Self-Portrait* (1899). The results indicate that data collected in the SWIR spectral range were adequate to differentiate, characterize and map the distribution of the different blue pigments on the paintings.

As the possibilities for image manipulation and analysis are somehow unlimited with MSI, reflected IR and UV

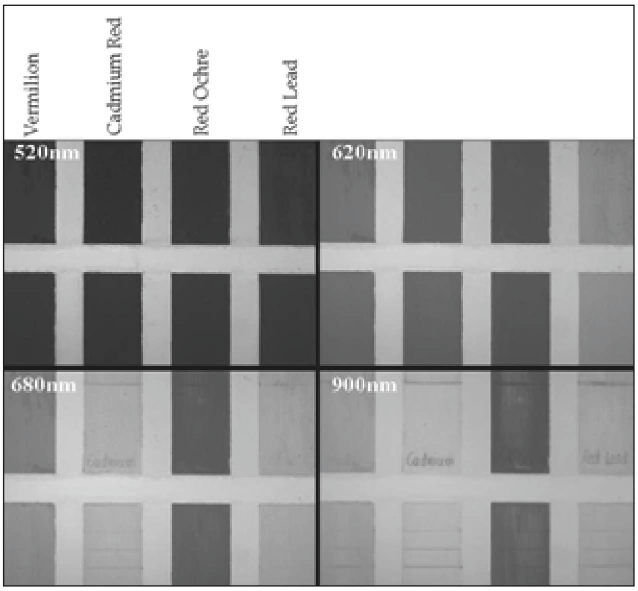

Fig. 3a Spectral images at narrow spectral bands (520, 620, 680 and 900 nm) of a custom-made reference pigment chart illustrating four different red pigments (Kakoulli 2003)

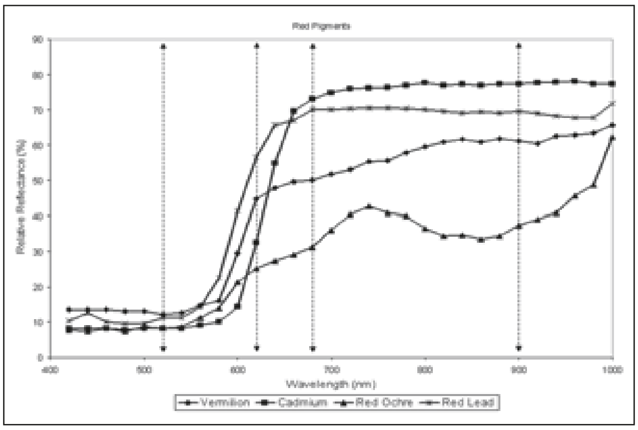

Fig. 3b Reflectance spectra of the pigments illustrated in Figure 3a. Comparing Figure 3a and their corresponding spectra, it can be observed that variations in reflectance as a function of the wavelength for each individual red pigment is correlated with the tonal intensity (transparency) of the images at the specific wavelength. For example, the reflectance of cadmium red clearly increases with the shift from 620 to 680 nm as shown in both the image and the reflectance spectrum. In contrast, red ochre remains non-reflective at the same wavelengths

false-color imaging have found useful applications for the characterization of materials [50, 96]. Spectral imaging provides a more flexible system for false-color imaging than conventional photography as monochromatic or combined infrared or ultraviolet bands can be specifically selected to create a pseudo-color image, based on the materials to be imaged, that achieves maximum differentiation. Aldrovandi et al. [50] used false-color infrared imaging to map successfully previous repaintings on a thirteenth-century tempera painting *Madonna with Child and Angels* attributed to Maestro della Maddalena. Similarly, the application of false-color reflected UV indicates a clear differentiation of white pigments in the painting *Mercato* from the Galleria d'Arte Moderna of Palazzo Pitti in Florence, painted by Elisabeth Chaplin in the 1930s [96].

Mansfield et al. [56] and Attas et al. [57] applied false-color MSI to examine two works of art, the drawing *Untitled (The Holy Trinity)* and the oil painting *The Mocking of Christ* from the Winnipeg Art Gallery (Table 1). The spectral imaging analysis of the drawing shows four different media. This was demonstrated using two different methods. In the first method [56, pp. 64–66] false-color infrared images were created by assigning a single-wavelength infrared image to each of the red, green and blue channels that make up an RGB image and displaying them simultaneously. In the second method, Attas et al. [57, pp. 131–133] combined three infrared images using PCA. These processed images contain important information from individual components and therefore display an enhanced image of the different media used for the drawing.

The mixed results obtained for the identification of pigments and their admixtures show clearly the current limitations of spectral imaging for this application. This can be attributed primarily to the restricted spectral range and to the non-availability of an exhaustive database of the reflectance spectra of pigments. The current lack of a pigment spectrum database indicates that it is a challenge to resolve the spectra of pigment mixtures into their single components. Although enhanced discriminating capabilities are expected with future technological developments, complementary and often invasive techniques requiring micro-sampling will still be needed to assist in the characterization of individual materials and pictorial layers.[1]

Study of documents and palimpsests

In 1994, a collaborative project between the Ancient Biblical Manuscript Center (ABMC), the Jet Propulsion Laboratory (JPL) and West Semitic Research (WSR) was launched with the aim of studying the Dead Sea Scrolls using spectral imaging technologies. When the results from MSI were combined with image analysis it was possible to reveal hitherto unreadable lines of the Dead Sea Scroll and make the script discernible [97].

MSI has also been applied to the study of palimpsests for the reconstruction and legibility of underlying scripts [36, 74]. One of the most celebrated studies concerns the Archimedes Palimpsest [98]. This important document in the history of mathematics was written on parchment during the tenth century and reused as a prayer book some 200 years later. The earlier script was erased, each page was cut in half, rotated 90° and overwritten. MSI at narrow spectral bands in the visible and long-wave ultraviolet, combined with image analysis utilizing special algorithms, assisted in enhancing the earlier script. However, there were limitations in areas where mould was present, while considerable time was required for computational processing [99].

Further research on palimpsests was carried out through the project, *Rinascimento Virtuale,* part of the European Program 'Culture 2000' [100]. In this project, MSI using various instruments assisted in the legibility of lower

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[1] The most commonly used invasive techniques in art conservation include polarized light microscopy (PLM), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX), X-ray diffraction (XRD), Raman micro-spectroscopy and FTIR.

scripts that had been previously difficult or impossible to read, based on target spectral differences. However, palimpsests with scripts of similar spectral signatures are still problematic. PCA and other data-processing methods are currently being evaluated for ways of producing a better differentiation and enhancement of the underlying, erased script. Scholten et al. [74] employed a monochromatic tuneable light source at wavelengths between 380 and 1100 nm and a monochrome high-resolution digital camera to record spectral cubes from various documents to assist in the characterization of inks and the readability of texts. Based on the spectral signatures of the different inks, their differentiation and mapping could be achieved using false colors. Faded scripts were enhanced and became legible by applying the Spectral Angle Similarity (SAS) technique on selected spectra.

Study and differentiation of organic binding media

MSI using UV-induced VIS-fluorescence[2] imaging has been employed for the differentiation of organic binding media as certain materials show different intensities and colors of fluorescence that can be useful for their identification. Applications of this technique to the study of the painting *Labela di Palma* achieved an unambiguous differentiation of white pigments, indicating a later repainting not visible to the naked eye [36, p. 334].

Kakoulli [101] used the same technique for the differentiation and characterization of organic materials in wall paintings. The results of this analysis show that the observed fluorescence emission of organic binding media was influenced by the technique and preparation of the substrate and by the pigments used in the paint. A decrease in the intensity of the fluorescence (fluorescence quenching) was observed in paint films where iron hydroxide and copper carbonate pigments were mixed with organic binding media such as linseed oil and rabbit skin glue. The results were correlated with standard reference samples and published data [102].

Other non-invasive techniques have been used for the characterization of organic binding media with varying degrees of success, including fluorescence lifetime imaging (FLIm), FORS, and Fourier transform infrared (FTIR) spectroscopy [103]. Research results obtained with these techniques for the characterization of organic materials in wall paintings were presented during the symposium organized by the Getty Conservation Institute held at the Venaria Reale, Torino in May 2006 [104].

Study of minerals and gems

Multi- and hyperspectral imaging has also been used for the analysis of semi-precious and precious stones. Gurschler et al. [43] have tested the capabilities of a HSI system equipped with a PGP to differentiate real turquoise from fake. PCA and FCM clustering analysis were successfully applied to the image cube to differentiate real turquoise from other minerals. However, samples of pressed, powdered turquoise could not be discriminated. Recently, Weiping et al. [64] have applied MSI and PCA for the classification of emerald and were able to separate metamers based on their spectral signature and overcome limitations posed by colorimetry.

Monitoring and evaluation of conservation treatments

MSI has been used for the evaluation of conservation treatments, mainly the assessment of laser ablation cleaning of artifacts. Kautek et al. [105] first published results on the use of MSI in the 320–1550 nm spectral range for the evaluation of laser cleaning on paper and parchment. The visible range allowed the accurate documentation of the color appearance before and after laser treatment, while in-depth and surface chemical modifications could be traced with the infrared and fluorescence in the visible light region. In a study on manuscripts, MSI helped to reveal surface alterations at 380 nm using ultraviolet reflectance imaging and it also enhanced in-depth damages at longer wavelengths [36, p. 336]. Pouli et al. [58] used MSI to assess real-time laser and micro-air abrasive cleaning methods for the removal of encrustations on archaeological marble; and the best results were obtained using ultraviolet reflection imaging around 365 nm. By determining the histogram threshold, segmentation of the areas with the same absorption characteristics was performed and over-cleaned areas could be mapped [58, p. 341]. The use of ultraviolet and infrared spectral imaging also assisted in the evaluation of color and textural modifications following laser cleaning of marbles [59, 60].

For the conservation of paintings MSI combined with a spectral matching algorithm using a dataset of reference spectra has been applied to the evaluation of pigment combinations to be used for inpainting or retouching and to solve issues of metamerism [92]. The MSI systems developed within the VASARI[3] and CRISATEL[4] projects described in the next section have also been used successfully during conservation treatments on paintings [71, 106] and the detection of damage to paintings during transportation [107].

Digital imaging for documentation and archiving

Documentation based on imaging has always been a key process for the management and conservation of museum and gallery collections and, until the advent of digital imaging, was carried out using conventional photography. A recent survey involving more than 50 American cultural heritage institutions has shown that over half took at least 90% of their photographs digitally in 2004, a majority using high-end cameras [108]. Owing to the tremendous development of digital technology during the last two decades, spectral imaging has naturally found useful applications and developments in this field.

In the late 1980s, at the dawn of digital era, the National Gallery in London together with a consortium of European universities, institutions and companies started a pioneering project to develop a digital imaging system for the scientific documentation of works of art, primarily

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[2] Emission of energy in the visible when materials are excited by UV light.

[3] Visual Arts System for Archiving and Retrieval of Images

[4] Conservation Restoration Innovation Systems for image capture and digital Archiving to enhance Training Education and lifelong Learning.

paintings, with high resolution and high color accuracy. Thus the VASARI project was born, followed over the years by others, such as the MARC[5] project. The imaging systems developed within these projects have been reviewed elsewhere [67, 68] and only the VASARI system is briefly described here. The MARC system [109], despite remarkable performances in terms of resolution and digitizing time, is based on a trichromatic camera without multispectral capabilities *per se*.

The first VASARI imaging system, completed in the early 1990s, was based on a monochrome camera equipped with a 500 × 290 pixel CCD array and a set of seven broadband filters covering the 400–700 nm spectral range. Both camera and lighting unit were mounted on a computer-controlled positioning system, allowing the scanning of paintings of up to 1.5 × 1.5 meters in size [110, 111]. The first two VASARI systems were operational at the National Gallery and the Doerner Institute in Munich and were capable of recording images with a size of about 10000 × 10000 pixels. The high resolution was achieved by means of a sensor-masking micro-positioning device able to record sub-images with a size of 3000 × 2820 pixels. The final set of images was obtained by mosaicing the sub-images, and the whole process required about three hours. Initially developed for scientific research purposes, especially for the monitoring of color changes in paintings over time [112, 113] the VASARI system has been mainly and very successfully used for documentation and archiving purposes [68].

Despite its obvious limitations such as lack of portability and time-consuming procedure, the VASARI system has remained unrivalled in term of resolution, although in the late 1990s most of the digitizing work of paintings was carried out with the faster and even higher resolution MARC systems [67, 109, 114]. More recently, two other spectral imaging systems were developed within the CRISATEL project framework, one at the National Gallery in London [71] and the other in Paris. The latter system is based on a vertical linear array CCD scanning camera producing digital images with a size of 12000 × 30000 pixels and is equipped with thirteen broadband filters: ten for the visible and three for the NIR [70, 115]. The system is capable of digitizing paintings up to 2 × 2 meters and is currently operational at the Musée du Louvre.

Notwithstanding the invaluable contribution of these projects to the field, the underlying technologies were unfortunately only accessible to institutions with the necessary resources. Moreover, the VASARI system, while integrating a set of filters, cannot really be described as multispectral because the multispectral information has only been used for accurate calibration and direct mapping to a standard CIE[6] color space. This was pointed out by Imai and co-workers [116], since it has been shown that color management based on spectral properties of materials is the only way to ensure accurate color reproduction and address essential issues such as metamerism [61, 117–120]. Knowledge of the spectral reflectance properties associated with each pixel in a digital image of a painting has also opened up innovative applications, allowing, for example, the virtual restoration of original colors or simulations of varnish removal – techniques especially useful to the conservator [61, 62, 69]. However, if spectral imaging has undeniably found its place in research areas related to digital documentation, the necessary parameters of the system, which would optimize both spectral and spatial information while fulfilling other practical requirements specific to this application, still need to be defined.

This goal has led to an impressive amount of research focused mainly on spectral reconstruction techniques [82, 121–123] and on the performance evaluation of multispectral systems with different configurations of filters in association with commercial- and research-grade digital cameras [40, 61, 73, 116, 119, 124, 125]. Moreover, as human perception is a critical factor for the quality assessment of color images, cognitive aspects have been researched as well, with the implementation of psychophysical experiments in which results of different multispectral technological approaches were evaluated from the perspective of the human eye [126].

No definite and unique solution has emerged yet from this research and this is not really surprising as spectral imaging in this application, as in others, can be considered as a cutting-edge technology still at the research stage. However, encouraging results have been obtained with a system based on a RGB array sensor with a limited number of broadband filters [127]. There are no doubts that in the near future an affordable multispectral system will be available, making it accessible to a large number of museums and institutions.

New perspectives and future directions for research

Although MSI and HSI technology have broadened the possibilities of imaging and materials' characterization, there are still limitations to be overcome for the systems commonly used in conservation. Most of the MSI systems described previously operate in the VNIR spectral range and, when characterization and mapping of materials is the main target, the VNIR offers limited possibilities. The potential of extending the capabilities of a MSI system to other spectral ranges, especially the SWIR, has been mentioned by several authors [52, 63, 73]. Indeed, this spectral range could be extremely useful to the conservation field as it allows the identification of a large number of inorganic and organic materials which do not show discriminative features in the VNIR part of the electromagnetic spectrum, which could, for example, help to remove some of the difficulties posed by the analysis of pigments and their admixtures.

From a technological point of view, InGaAs cameras with a cut-off wavelength at 1.7 µm are not well-adapted for the study of materials of historic and artistic value as most of the discriminative spectral features are located between 1.5 and 2.5 µm. However, InGaAs FPAs extended to 2.5 µm should soon be commercially available. Moreover, if criteria such as portability and operability are added to the system requirements, a camera based on a SWIR–MCT detector is probably the best candidate,

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[5] Methodology for Art Reproduction in Colour

[6] Commission Internationale de l'Eclairage

mainly for a spectral imaging system for field conservation, and recent technological advances allow us to envisage such developments at a reasonable cost in the coming years [128–130]. Indeed, the real technological challenges will probably lie in the development of adapted dispersing devices and the integration of all parts of a system in a compact and portable design.

As already mentioned, the SWIR spectral range has long been used in satellite and airborne remote-sensing applications as well as for field and laboratory reflectance spectroscopy measurements, especially for the management of terrestrial natural resources and in the planetary sciences [14, 15, 131, 132]. Among the results obtained in remote sensing of particular interest to conservation are those relating to the identification of minerals and rocks [133–137], the mapping of mineral alteration sequences [138–141], the properties, water content and salinity of soils [142–145] and the identification of bio-organisms [146–149].

In the context of conservation-oriented applications, these results open new perspectives for the identification and mapping of other materials beside pigments, such as stone, mortars, salts and organic compounds. Moisture distribution in porous materials, often investigated with thermal infrared imaging technology [150, 151], could be mapped as well using MSI in the SWIR range.

Potential applications for conservation could include:

- assessment and monitoring of the state of deterioration of monuments and archaeological sites
- monitoring of conservation treatments
- study of patinas and biodeterioration features
- identification and sourcing of archaeological artifacts
- investigation of stone sculptures for authentication
- identification of pigments and binding media in paintings

Conclusion

This review has shown that spectral imaging technology that combines non-invasive analytical capabilities and imaging should become a powerful tool for both conservators and conservation scientists. The fact that the technique, despite its current limitations, has already found various successful applications in conservation reflects its potential. However, this wide range of applicability has also shown that the requirements for a spectral imaging system, in terms of camera resolution, spectral range and resolution, are application-dependent. This depends on whether more emphasis is put on the imaging or the spectral component, considering the data as a stack of wavelength resolved images or as a series of spatially resolved spectra. For example, a high-resolution camera is a primary criterion for good quality images in documentation, whereas for pigment identification in paintings, spectral range and number of bands are critical parameters for resolving spectral features. Future developments will be closely linked to the specific needs of each application.

For material identification and mapping, the expected development of SWIR multi- and hyperspectral systems, combined with the existing VNIR and possibly UV extended systems, should make the technique a useful method for both outdoor (monuments and archaeological sites) and indoor (conservation laboratory and museum) investigations. The novel capabilities of MSI and HSI techniques, combining imaging and spectroscopy, will therefore be valuable in complementing other non-invasive techniques of investigation. Furthermore, spectral imaging could also be used to guide and optimize sampling procedure when invasive analytical techniques would be otherwise required for the characterization of particular materials and for the study of cross-sections under the microscope to create distribution maps of individual particles and layers based on their spectral characteristics.

Advances in the spectral capabilities of the instrumentation, in terms of both resolution and spectral range, will however require the development of specific research directed towards conservation-oriented applications. For example, studies in reflectance spectroscopy on reference materials, the creation of a spectral database and research on automated post-processing methods (including spectral derivative analysis and multivariate statistics) can be considered indispensable for the interpretation of the large amount of data generated by MSI and HSI technologies. The implementation of this research will help to build the necessary knowledge base and utilize the full potential of this innovative and fast-developing method of investigation, thus providing the greatest benefit to the conservation community.

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