

A novel hyper-spectral imaging apparatus for the non-destructive analysis of objects of artistic and historic value

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Abstract

We have developed a computer controllable hyper-spectral imaging apparatus, capable of acquiring spectral images of 5 nm bandwidth and with 3 nm tuning step, in the spectral range 380–1000 nm. The critical component of the apparatus is the innovative imaging monochromator, which enables the tuning of the imaging wavelength. This module is coupled with a two-dimensional detector array composing a tunable wavelength camera system. Electronic controllers are employed for detector and monochromator synchronization and driving, while the system calibration, image processing and analysis are performed with the aid of specially developed software. The system records light intensity as a function of both wavelength and location. In the image domain, the data set includes a full image at each individual wavelength. In the spectroscopy domain, a fully resolved diffuse reflectance and/or fluorescence spectrum at each individual pixel can be recorded. The developed spatially resolved spectral acquisition system is ideal for the non-destructive analysis of heterogeneous materials such as objects of artistic and historic value. Experimental studies show its potential in assisting the identification and mapping of painting materials in situ. Furthermore, it was shown that it enables the recovery of erased–overwritten scripts in old manuscripts and the determination of proper spectral bands for the on-line monitoring of laser and non-laser cleaning procedures. © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

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1. Introduction

Macroscopic-technical examination and documentation of objects of artistic and historic (A&H) value employ a variety of methods and techniques, ranging from simple visual examination to specialized film and/or electronic imaging. The latter typically include image capturing and analysis in broad spectral bands within the ultraviolet (UV)–visible and near-infrared (NIR) regions of the spectrum, using a plurality of different detectors and cameras [1,2]. If macroscopic-chemical and structural information is required, then invasive sampling and ex-situ analysis are undertaken. Invasive investigations have the drawback of being harmful to the A&H object—as they require samples to be taken—and provide only point information that is not necessarily representative of the object area under analysis.

In an attempt to eliminate the need for diagnostic interventions, a variety of non-contact, in situ applicable spectroscopic techniques have been experimentally used over the last two decades. Established spectroscopic techniques such as (diffuse) reflectance (R), fluorescence (F), x-ray fluorescence (XRF), Raman (R), Fourier transform infrared (FT-IR), laser induced breakdown spectroscopy (LIBS) [3–7], etc., have been extensively applied and evaluated in the scientific analysis and documentation of A&H objects. The obtained results have shown that optical spectroscopic techniques are capable of providing a unique insight into the material composition, technique of construction, deterioration effects, etc., which are essential for the A&H analysis and helpful in determining the optimum preservation scheme. However, the above-mentioned techniques suffer from the major drawback that they are capable of acquiring spectral information from only one—visually selected—spatial point. As in the case of invasive sampling, point information is inadequate for the analysis of A&H

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objects, since they are characterized by high spatial heterogeneity. On the other hand, there are cases where alterations in the object's material status, associated with deterioration effects, interventions, etc., are not visually detectable. Due to this fact, point spectroscopic techniques based on the visually driven probing, cannot be used for the detection and identification of incipient deterioration effects, non-visible restoration interventions etc.

These limitations highlight the need for the development of spatially resolved spectral acquisition methods and technologies, capable of performing spectral mapping of the area under analysis. If the acquired spectra contain molecular specific information, then spectral mapping could optimally result in the in situ mapping of the chemical composition of the material. Such information is provided by Raman, FT-IR and LIBS spectra. In the case of LIBS, which is based on the spectral analysis of the plasma, generated with laser ablation of the material, it is not possible to realize spectral mapping without the point-by-point destruction of the surface under analysis. Raman and FT-IR are non-destructive and due to their operational characteristics (point excitation and probing), spectral mapping can be obtained with the spatial scanning of their illumination-detection module. However, due to the quite small size of the light spot used for material excitation, spatial scanning can cover very small areas within reasonable time periods. For this main reason, spectral mapping can be realized only in microscopy [3,6] and the technique is applicable mainly in ex-situ analysis.

Although the extraction of the diagnostic information from reflectance and fluorescence spectra is not straightforward, these techniques have the advantage of being non-destructive and easily applicable in situ. Moreover, the efficiency of the process is high and the resulting optical signal strong, so no point excitation and probing and spatial scanning is required in order to obtain spectral mapping. Large areas can be illuminated and imaging detectors can be employed to capture two-dimensional reflectance or fluorescence data within the detector's field-of-view. There is a great flexibility in selecting the size of the latter, since it is solely determined by the operational characteristics of the coupled lenses, microscopes, etc. Spectral information can be obtained by developing and implementing imaging monochromators, which operate as a tunable optical filter. This configuration comprises an advanced diagnostic technology, where the advantages of both imaging and spectroscopy are fully exploited. Nevertheless, diffuse reflectance and fluorescence spectra of A&H objects, captured in the visible and near-visible, UV and IR spectral ranges, are usually broad, being the result of the broad emissions of a great number of different molecules. Due to this fact, the measured spectra include limited diagnostic information since they are not molecular specific and include convoluted information for the materials used to develop the A&H object. However, it is possible to improve the obtained diagnostic information by developing material samples that

emulate all the possible combinations of materials used to develop the A&H object and compare their diffuse reflectance and/or fluorescence spectral characteristics with the ones acquired from the original H&A object. In this approach, material samples and their spectra comprise a calibration or training set for the diagnostic procedure, facilitating the identification of unknown materials.

Another important consequence of the combination of imaging with spectroscopy is that it comprises a powerful, artificial vision tool, since it enables the inspection at narrow spectral bands, in a wide spectral range and the direct assessment of invisible or low contrast features of diagnostic importance. Based on the above considerations, it seems that reflectance and fluorescence spectral imaging and spectroscopy, combined with computational methods for spectral analysis and comparison, hold the promise to become a valuable diagnostic tool.

We present a novel hyper-spectral imaging (HySI) system developed at Forth-Photonics, which features a notably improved spectral and spatial resolution. We also present results from the pilot application of this imaging system in the identification and mapping of painting materials in situ, in reading palimpsests and in visualization of coatings in order to assist the on-line monitoring of artwork cleaning procedures.

2. Experimental methods

2.1. Spectral imaging technology: background

In an attempt to develop advanced spectral imaging systems with advanced diagnostic capabilities, a number of technological solutions have been presented and used in a variety of remote analysis applications. In the field of art and cultural heritage, the diagnostic tasks are complicated, and due to this fact, the demand for multipurpose, high-end spectral imaging devices is increasing. In response to this demand, various imaging systems that are based on either illuminating or imaging monochromators have been developed and used for the non-destructive analysis and documentation of A&H objects. In the case of illuminating monochromators, the technology employed is trivial, comprising a light source and a set of band pass optical filters that are interchanged in the path of the light beam that illuminates the object [8]. Then a general-purpose camera is used to capture the spectral image(s). Although simple, the spectral illumination approach suffers from the drawback that the image capturing procedure is randomly affected from the ambient light conditions. Moreover, systems based on this configuration cannot perform fluorescence spectral imaging.

An optimum set-up for the acquisition of multiple spectral images is the coupling of imaging detectors with imaging monochromators. MuSIS-2007, developed by Balas [9,10] at FO.R.T.H., is a representative multispectral

imaging system, which is specialized for the in situ, non-destructive analysis of A&H objects. The MuSIS-2007 imaging technology enables the integration of a plurality of imaging modes (reflectance, fluorescence) and spectral bands, ranging from UV to NIR in one camera system. Although of relatively low spectral resolution, this configuration has demonstrated great diagnostic potential.

The development of high spatial and spectral resolution imaging monochromators and devices, known as HySI, will result in a notable improvement in the obtained analytical and structural information. Although significant achievements have been reported during the last 10 years, this demanding scientific technological field continues to attract the interest of several interdisciplinary research teams. Typically the hardware of a HySI system comprises an imaging detector, coupled with a special imaging monochromator, while both are interfaced with personal computer and controlling units. The HySI monochromator operates as a tunable narrow band pass optical filter, enabling the inspection and capturing of numerous narrow spectral band images across its tuning range or, if tuning spectral resolution is high, a full spectrum per image pixel. The available imaging monochromators have been tailored to comply with the needs of a variety and diverse applications, ranging from astronomy to microscopy. They implement different technologies according to which they are categorized. Particularly, there are three main categories of imaging monochromators: the acousto-optic tunable filters (AOTF), the liquid crystal tunable filters (LCTF), and the Fourier transformed interferometers (FTI) [11,12]. Imaging devices based on the above-mentioned technologies have found interesting applications mainly in microscopy and have several important perspectives in the analysis of A&H objects. However, several limitations associated with their operational characteristics have been reported such as narrow tuning spectral range (AOTFs, LCTFs), low throughput (AOTFs, LCTFs), image shifting during wavelength tuning (AOTFs), non-real time spectral imaging (FTI), time consuming procedure (FTI). Moreover, the relevant instrumentation is in all cases expensive, delicate and complicated. These technological limitations in several cases prevent the applicability of these technologies in the in situ analysis of A&H objects. In particular, limited diagnostic information is obtained due to their narrow tuning spectral range, since different modules are required to cover either the visible or the NIR spectral range. Moreover, the low throughput of these systems necessitates the use of a high power light source for the illumination of the object in order to obtain acceptable image brightness. But this could be harmful for the object, since high power illumination can provoke photo thermal and/or photochemical damage. Furthermore, due to the low throughput it is very hard to record weak fluorescence signals in narrow spectral bands.

The above-mentioned drawbacks and limitations of the existing technological approaches, in combination with the demanding diagnostic problems met in the analysis of A&H

objects, highlight the need for the development of an advanced HySI system capable of combining the following operational characteristics: (a) real time spectral imaging for inspection and focusing, (b) high spectral resolution and wide spectral range, (c) operation in both reflectance and fluorescence spectral imaging modes (d) high throughput and sensitivity in order to avoid long exposure times and intense light excitation, which is in several cases harmful for the object.

2.2. Novel hyper-spectral imaging apparatus: operational characteristics

In an attempt to approach the above-mentioned diagnostic performance, we have developed a HySI system, based on a patent pending, all-optical imaging monochromator, which is illustrated in Fig. 1. Displacement of the optical elements of the latter results in the tuning of the imaging wavelength, which is performed with the aid of electro-mechanical manipulators, is controlled from the PC via microcontroller. The system is capable of acquiring spectral images of 5 nm full width half maximum (FWHM), with 3 nm tuning step, in the spectral range 380–1000 nm. The minimum transmittance is 40% across its operational spectral range, which determines the high throughput of the developed monochromator. The tuning spectral range matches the responsivity spectral range of the charge coupled device (CCD) image sensor but it can be extended for longer wavelengths, up to the mid-infrared range. The output feedback signal of the monochromator carries information for the state of the tunable filter, thus enabling its synchronization with the image capturing procedure. The monochromator is interfaced with a black and white, megapixel CCD camera, based on the IEEE-1394 data transferring protocol, capable of acquiring images at a rate of 15 frames/s at full resolution and of more than 30 frames/s at VGA resolution.

Specially developed software, which is compiled under turbo C++, is employed for the control of the camera and monochromator as well as for the spectral image analysis. The system operates in two modes: the spectroscopy mode



Fig. 1. The novel hyper-spectral imaging (HySI) apparatus.

and the spectrometry mode. The former enables the random selection and real time visualization of desired spectral images, while the spectrometry mode performs synchronized spectral scanning and image capturing and, finally, calculation of one full spectrum per image pixel. In both cases, a special calibration procedure [13] is executed before these imaging procedures, in order to compensate for the wavelength dependence of the response of the electro-optical parts of the system, such as CCD, illuminators, etc. A Ba_2SO_4 white plate with unity reflectance across the 380–1000 nm spectral range is used as a calibration specimen. The specimen is placed in the field-of-view of the lens and the gray value of the central area of the image is real time displayed. Then the monochromator scans the total spectral range and in each tuning step the camera shutter and gain is automatically regulated so that the displayed gray value approaches the value of 255. This ensures that the dynamic range of the CCD is fully exploited. The shutter and gain values, used to obtain 255 gray level, are stored in each wavelength-tuning step, together with the image of the white specimen, constituting the calibration data set of the system. These settings determine the sensitivity level of the camera, which increases as the imaging wavelength is tuned to shorter or to longer wavelengths than the wavelength range at which the maximum light throughput and efficiency of the system is obtained. This makes the system's response almost independent from the wavelength, thus ensuring a "device-independent" spectral imaging and spectrometry. The stored spectral images of the white specimen are used in order to correct for the uneven of image brightness due to the non-uniform transfer function of the optics (flat field correction). By running the spectrometry code section, the system performs synchronized tuning of the imaging wavelength and image capturing and storing of the area under analysis. In each step, the sensitivity of the camera is automatically regulated according to the stored, during calibration, shutter and gain values. From the stored stack of spectral images, a spectrum can be calculated from the gray values of the corresponding pixel spectral column and displayed for any spatial point of the image. The spatial resolution of the detector determines the number of the spectra that can be collected in one experiment run. With the described configuration, 1 000 000 spectra can be collected in approximately 2 min scanning time. The system also embodies a fast saving procedure at a lesser (VGA) resolution, which reduces the scanning time of the system to 10 s.

The identification of original and added material (e.g. pigments, binding media, coatings, retouching) is essential for dating and authentication of the artwork and contributes significantly to our understanding of art objects. In addition, it facilitates the evaluation of the physical condition (deterioration, interventions) and directs conservation decisions. We present and discuss results from the pilot use of the described system in the recovery of erased and overwritten scripts in old manuscripts, in pigment identification and mapping, and in assessing laser cleaning effects.

3. Applications, results and discussion

3.1. Recovery of overwritten script

It was a common practice, particularly in medieval ecclesiastical circles, to rub out an earlier piece of writing by means of washing or scraping the manuscript, in order to prepare it for a new text. The motive for making palimpsests seems to be largely economic, since reusing parchment was cheaper than preparing new skin. Another motive may have been directed by the desire of Church officials to "convert" pagan Greek script by overlaying it with the word of God. Modern historians are usually more interested in older writings and in this context we are developing methods and technologies based on HySI and digital image analysis in an attempt to recover erased old texts.

Fig. 2 illustrates a series of selected spectral images of a detail of a palimpsest, dated from the 11th century AD, where an earlier handwriting has been overwritten with a red ink. It is clearly seen that the shorter than 580 nm wavelengths are highly absorbed by the ink of the overwritten letters (appear dark), thus preventing the visualization of the underlying script. For longer than 580 nm wavelengths, the red ink becomes progressively transparent as the imaging wavelength increases. In this particular case, we have shown that for longer than 700 nm even the earlier script becomes also transparent. As it is seen in Fig. 2, there is a critical wavelength (600 nm) at which the optimum result is obtained. At this wavelength, the earlier script is best recovered, which, as it is seen, is a capital-letter script. Further enhancement of the obtained contrast can be achieved by applying digital image analysis methods and algorithms. It is obvious that the latter would be of limited effectiveness if they have been applied to regular color images or to images that correspond to shorter than 600 nm wavelengths. The presented findings indicate that by exploiting the spectral characteristics and differences between inks and substrates, one or more spectral bands can be determined at which the best result is obtained. The fact that historic manuscripts have been developed with various techniques using a variety of different materials that are additionally subjected to deterioration alterations, suggests that the optimum imaging wavelength(s) will be different from case to case. The described HySI enables the selective imaging and recovery of manuscript letters and of other important features in a variety of different cases, since it enables the fine-tuning of the imaging wavelength in a wide spectral range.

3.2. Pigment identification and mapping

Spectral imaging and analysis was performed for the identification of the red paint of the initial letter T of an illuminated manuscript dated from the 12th century AD, which is illustrated in Fig. 3(A). A full series of spectral images of the red paint, included in the rectangle, were collected in

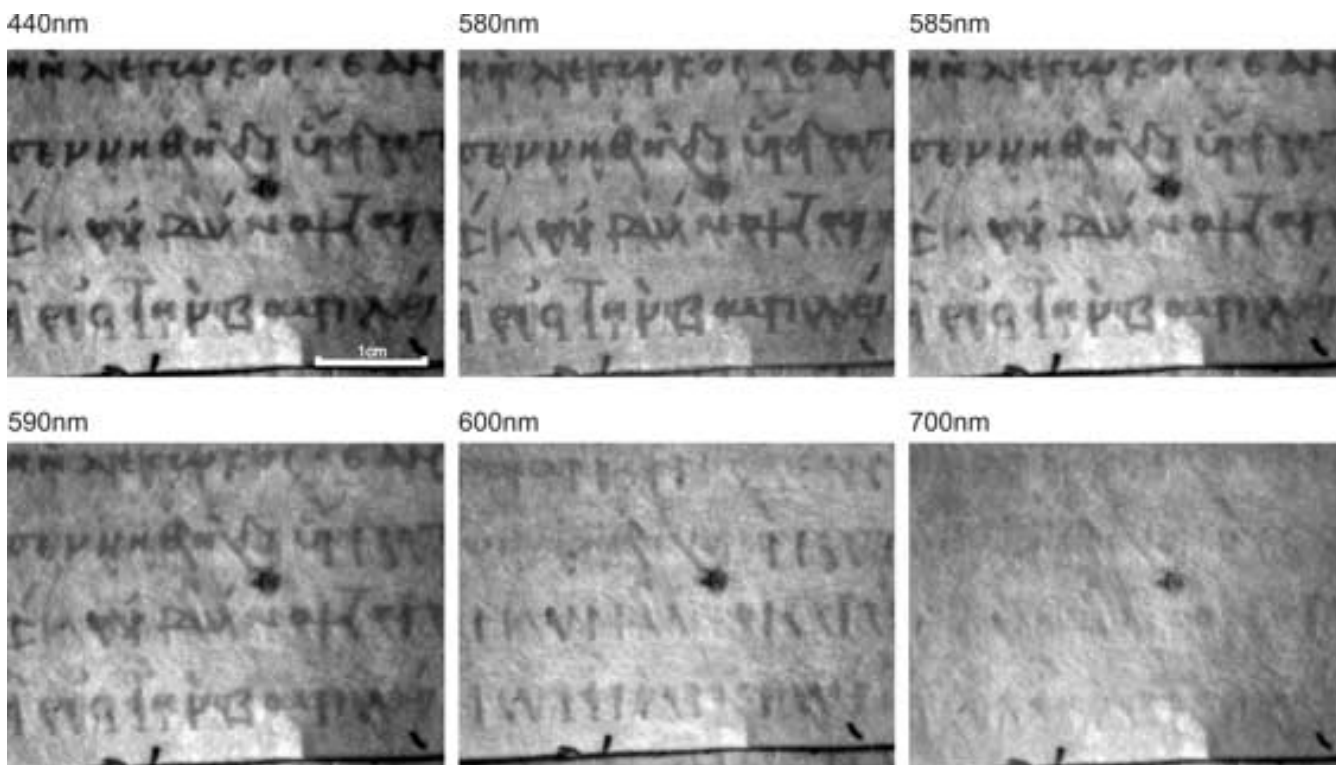


Fig. 2. A detail from a palimpsest captured at different narrow spectral bands. For longer than 600 nm, the overlaying letters become transparent.

direct comparison with model samples of vermilion, mars red (red iron (III) oxide, Fe_2O_3) and cadmium red (cadmium sulfide selenide, $\text{CdSe}_{1-x}\text{S}_x$). This was performed in order to ensure identical imaging conditions for both the manuscript and the reference samples. Before image capturing, the system's calibration was carried out as described above. A full set of spectral images was collected and images corresponding at selected wavelengths selected are shown in Fig. 3(B) together with reflectance spectra (Fig. 3(C)) of the model samples calculated from the stored spectral image stack. It is clearly seen that the variation of reflectance as a function of the wavelength of the red paint on the manuscript matches quite well with that of vermilion in the reference sample, while it is in clear contrast with that of mars red. More specifically, the reflectance of the red paint and of the vermilion sample appears both to increase similarly above 580 nm as indicated in the images shown. The dark shade due to the red paint faints as the imaging wavelength shifts from 570 to 600 nm. On the contrary, the mars red sample remains highly non-reflective up to 620 nm as clearly seen in the corresponding image. Cadmium red, on the other hand, has an intermediate behavior showing an increase in reflectance above 610 nm as seen in the 610 and 620 nm images, which is also depicted in the diffuse reflectance spectral data (Fig. 3(C)).

Another example dealing with pigment identification in painting using fluorescence spectral imaging is presented below. The illustrated detail of the painting "Labela di Palma" (Fig. 4) includes a retouching performed with a white paint, which is not seen in the visible reflection image

(Fig. 4). In order to recover and identify the retouching material, white material models were developed for spectral comparison, which include, from left to the right, lead, titanium, lithopone and zinc white and are shown in the upper part of the spectral images. Any attempt to differentiate these white specimens based on their diffuse reflectance spectra was unsuccessful, due to the fact that their spectral characteristics are almost identical in the 380–1000nm spectral range. As an alternative approach, the hypothesis that they could have different fluorescence characteristics was investigated. With the HySI system operating in the fluorescence mode, using a mercury lamp filtered to transmit 365 nm as excitation light source, fluorescence spectral images of both painting and material models were collected (Fig. 4). As it is seen in these images, the retouching is differentiated from the original background at 520 nm and for longer than 520 nm wavelengths, due to the fact that the former emits a stronger fluorescence signal in this spectral range. The comparative evaluation of the spectral variations of fluorescence intensity of the illustrated white samples with the ones of the original object shows that the retouching matches the fluorescence characteristics of the lithopone white model, while the fluorescence characteristics of the original background do not alter significantly with the wavelength, which matches the behavior of the lead white model. These comparisons strongly suggest that the original paint is lead white and the added retouching is lithopone white.

Through these examples, it becomes evident that with a carefully planned approach, the HySI analysis can provide

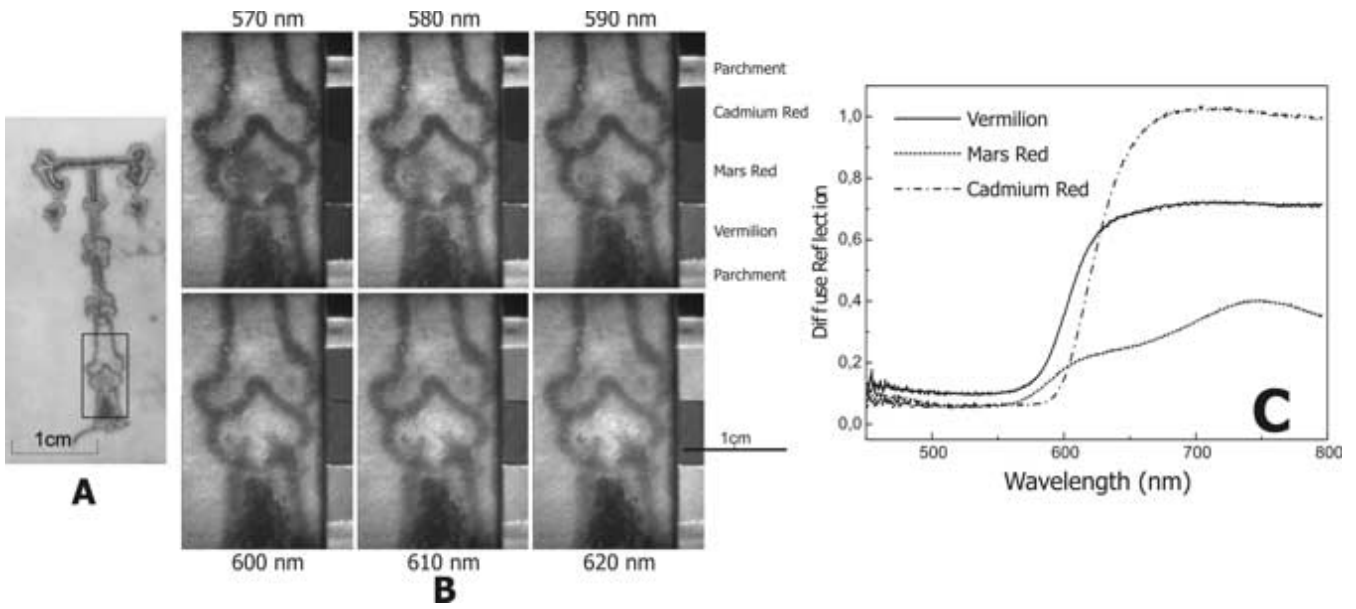


Fig. 3. A detail of an illuminated initial letter T (A) captured at several narrow spectral bands together with material models (right side) (B) and the calculated reflectance spectra (C) from the stored spectral images. Both visual and spectral comparisons indicate that the red ink is vermilion.

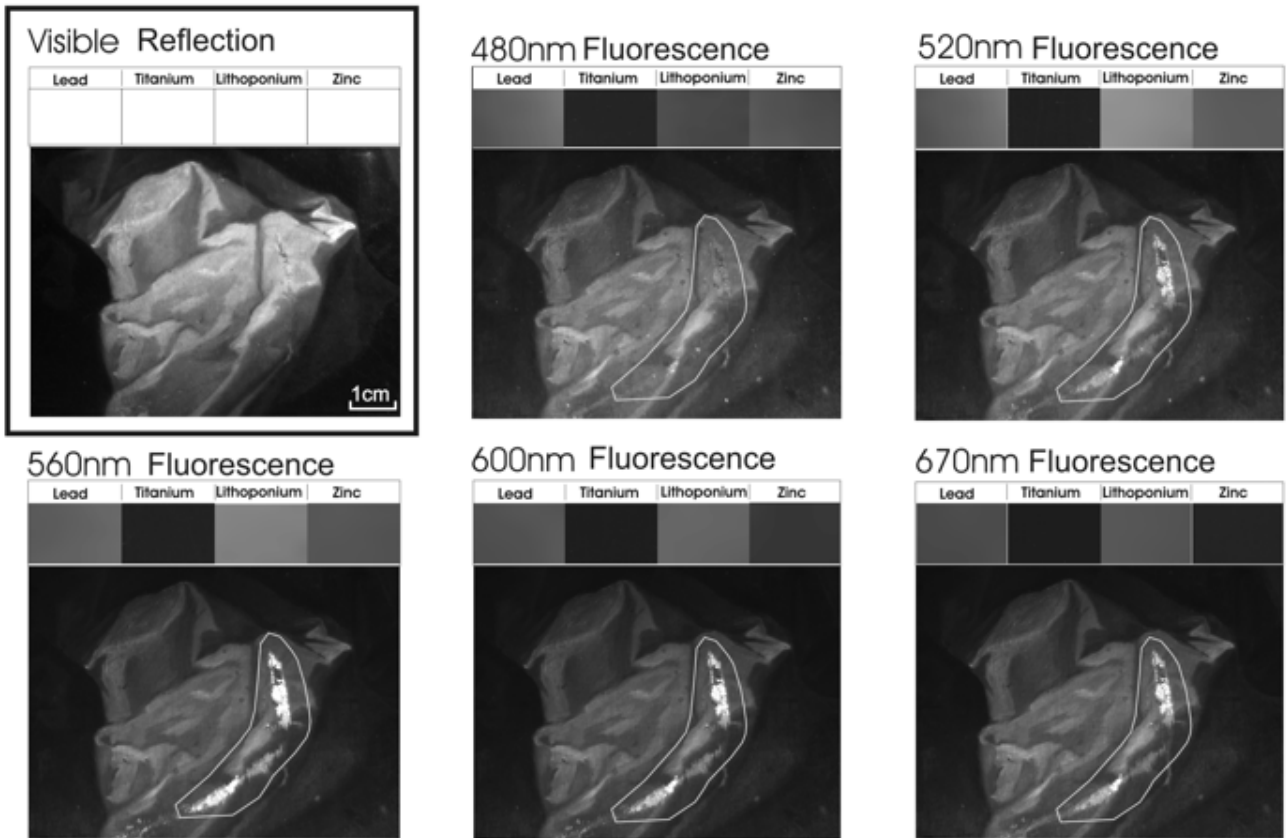


Fig. 4. Visible reflection image and fluorescence spectral images including white material models, an unknown original white paint and an unknown paint used to perform a retouching. The comparison of the fluorescence intensity variations as a function of the wavelength with the ones of the models suggests that the original paint is lead white, while the added retouching is lithopone white.

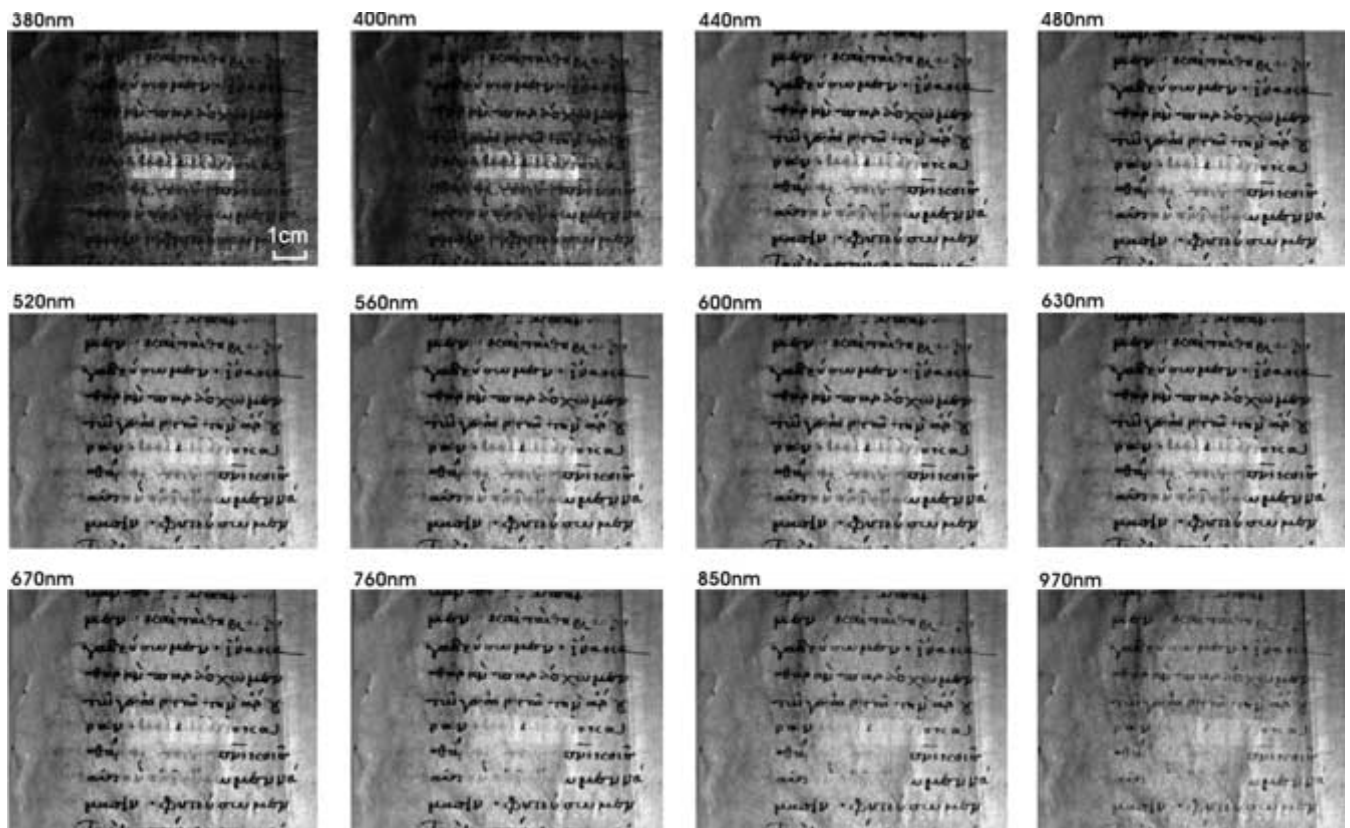


Fig. 5. A set of spectral images of a detail of an old manuscript cleaned with a 532 nm-second harmonic Q-switched Nd:YAG and an excimer laser. The Nd:YAG induced surface alterations are not seen in the visible, while they are well depicted in the 380 nm image. The captured spectral images also show an in-depth damage provoked by the excimer laser.

not only mapping but also identification of pigments. In this respect, it is important to combine computational algorithms for spectral deconvolution, such as neural networks and principal component analysis with the development of a database consisting of spectra obtained from a variety of pigments and mixtures of pigments in appropriate media and substrates, which closely simulate realistic objects examined.

3.3. Assessment of laser cleaning effects

Fig. 5 illustrates a set of spectral images of a detail of an old manuscript, cleaned with two different LASER beams. The larger square area, seen in the 380 nm image has been cleaned with the 532 nm-second harmonic of a Q-switched Nd:YAG laser with 0.5 J/cm^2 energy density and 10 ns-pulse duration. The smaller-whiter area has been cleaned with an excimer laser at 248 nm, with 0.8 J/cm^2 energy density, and 25 ns-pulse duration. The area cleaned with the 532 nm laser is visible mainly in the blue-UV band, while the area cleaned with the excimer laser remains visible even in the infrared band. This, in combination with the fact that blue-UV images include information mainly for surface features, while images captured at longer wavelengths carry information for deeper layers, suggests that excimer laser treatment provokes an in-depth damage of the manuscript.

In contrast, the Nd:YAG induced surface alterations are not detectable in the visible, while they are best depicted in the 380 nm image. This indicates that imaging at 380 nm provides a means for the more precise, on-line monitoring of the surface material removal. Research work is currently conducted to our labs, in an attempt to determine optimum imaging wavelengths for the on-line monitoring of cleaning procedures in a variety of application fields.

4. Conclusions

The developed HySI system comprises an integrated spectral imaging technology with several distinct advantages over the existing systems. It features wide operational spectral range-extendable up to mid-infrared, high spectral and spatial resolution and sensitivity, while it is capable of operating in both diffuse reflectance and fluorescence mode. Furthermore, it implements an innovative calibration method, which ensures the device-independent and reproducible imaging spectroscopy and spectrometry.

The essence of HySI is the fact that it produces superior data in the form of a large number of images, corresponding to different wavelengths across the spectrum, which in turn are used to obtain more than 1 000 000 spectra, each corresponding to an image point. This feature is valuable for

the analysis of spatially heterogeneous materials, since compositional information can be obtained for any spatial point of the object. The presented applications indicate that HySI has the potential to detect, identify and map the distribution of A&M materials—both original and added, based on their spectral characteristics, in a strictly non-destructive way. In several cases, it is possible to differentiate and identify A&H materials with similar coloration but of different chemical nature, by simply tuning the imaging wavelength, inspecting the narrow band images of both A&H object and material models and comparing their reflectance or fluorescence characteristics. The obtained differentiation is based on the provided superior spectral resolution in comparison with the three-color visualization and on the fact that in several cases different A&H materials with similar coloration have different spectral profiles outside the visible part of the spectrum. The diagnostic potential of HySI is open for further improvements such as implementation of spectral databases, digital image analysis and data processing algorithms such as neural networks and PCA.

Besides spectral mapping and compositional information, HySI enables the contrast enhancement between features under analysis and background, based on their spectral differences. This enables the recovery and extraction of valuable historic and artistic information. Furthermore, the capability in tuning the imaging wavelength enables the selective imaging of the different layers of A&H object, since the absorption coefficient of the materials used is in general wavelength dependent. Thus, by tuning the imaging band from UV to IR, selective imaging of different layers is obtained, since coatings are better visualized in the blue-UV area, while together with pigments they become transparent in the NIR band, allowing the observation of underdrawings, retouchings and pentimenti.

The presented indicative and diverse applications highlight the potential of HySI apparatus as a multipurpose system, useful in both research and practice in a variety of disciplines involved in field of analysis and preservation of A&H objects. The implementation of the developed imaging technology to this field will result in the improvement of the diagnostic capability, reliability, flexibility, in the reduc-

tion of both diagnostic and labor cost, while it will contribute significantly to the minimization of the destructive diagnostic interventions.

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