Università degli Studi di Padova
Dipartimento di Scienze Chimiche

SCUOLA DI DOTTORATO DI RICERCA IN SCIENZE MOLECOLARI
INDIRIZZO SCIENZE CHIMICHE
CICLO XXIII

APPLICATIONS OF IMAGING SPECTROSCOPY TO THE CHEMISTRY OF CULTURAL HERITAGE FIELD

Direttore della Scuola : Ch.mo Prof. Maurizio Casarin
Coordinatore d’indirizzo: Ch.mo Prof. Maurizio Casarin
Supervisore: Ch.mo Prof. Renzo Bertoncello

Dottoranda: Elena Paz Rebollo San Miguel

Abstract

The aim of this doctoral dissertation is to study the application of imaging spectroscopy to the field of chemistry for cultural heritage. In particular, the LUXOR Laboratory of the IFN-CNR has built in collaboration with the DEI department of the University of Padua a transportable imaging spectroscopy device. In the present work, the potentialities of such kind of systems for the analysis of works of art and archaeological artefacts, mainly focusing on the applications on the chemistry for the cultural heritage field will be examined and discussed. Study of cultural heritage objects present difficulties arising from the particular features of these samples: they are precious and sometimes unique pieces that required novel analytical non-invasive methodologies. Although some of the issues that will be treated are originated from the characteristics of the specific approach adopted, they can be regarded as general problems concerning imaging spectroscopy technique that still is in its early stages of development in this area. Therefore, the work can be considered of great interest for the scientific community dealing with cultural heritage issues.

Imaging spectroscopy (IS) extends the measurement domain of one-dimensional UV-VIS-IR spectroscopy to the two-dimensional domain providing information which can be used to characterize, to map and to monitor materials constituting works of art. It is a non-invasive technique and the developed measuring devices can be transportable. Considering the type of information acquired by this kind of system without sampling and contact, it seems obvious that this technique can represent a powerful tool for the cultural heritage field. The imaging spectroscopy device is built in order to acquire visible diffuse reflectance spectra of entire large-sized surfaces (up to 3meter wide). The collected data can be used to characterize, map and monitor materials constituting cultural heritage objects.

The main part of the work is focused on the development of a measurement methodology with the IS device to acquire reflectance spectra. For this purpose, different samples has been studied, including several that were prepared *ad hoc*. Different tests had identified some problems on the methodology that had been successfully resolved. Laboratory replicas of paint films were also prepared and exposed to accelerated ageing process several times. During this procedure, the samples were monitored with the IS device that was able to study the optical changes suffered by

the replicas. The results show that the developed measurement methodology with the IS device to collect reflectance spectra from 420nm to 850nm could represent a powerful analytical tool to characterize, differentiate, map and monitor painting materials (i.e. pigments). A similar procedure was employed to develop another measurement methodology with the IS device but in this case to collect spectra in transmittance mode in the same wavelength range. The purpose is to applied such method to study chromophores of glassy objects regarding the cultural heritage field as stained glass windows.

Both developed measurement methodologies has being applied to the examination of artefacts in order to demonstrate its potentialities to solve real analytical issues regarding the cultural heritage field. The reflectance methodology was applied *in situ* to the interdisciplinary study of a mural painting during its restoration process. The results had permitted the identification of most of the pigments employed to elaborate the artwork, some of the materials employed in the restoration and had showed the benefits of a multi-technical non invasive and portable approach using imaging spectroscopy and X-Ray Fluorescence. The measurements on transmittance mode were used to the simultaneous characterization of numerous coloured glass *tesserae* of stained glass windows. The analysis through imaging spectroscopy had identified several chromophores of the samples studied.

From the results obtained, imaging spectroscopy appears as an interesting and not fully exploited technique to study materials concerning cultural heritage objects. In the visible range, the principal application is upon the obtained results the characterization and/or differentiation, mapping and monitoring of pigments in paintings, manuscripts... However, due to its versatility it is also a powerful analytical tool to identify chromophores in glassy objects

Riassunto

Il proposito di questa tesi di dottorato è studiare le applicazioni della tecnica di spettroscopia ad immagine nel campo della chimica dei beni culturali. In concreto, il laboratorio LUXOR, struttura afferente all'IFN-CNR, in collaborazione con il dipartimento di ingegneria dell'informazione (DEI) dell'Università degli Studi di Padova, ha costruito uno strumento portatile che sfrutta la tecnica di spettroscopia ad immagine. Nel presente lavoro di dottorato, le potenzialità di questo tipo di sistemi per l'analisi di manufatti artistici sarà esaminato e discusso, focalizzando il lavoro principalmente nel campo della chimica per i beni culturali. Lo studio di questo tipo di oggetti presenta delle grosse difficoltà date le loro particolari caratteristiche. Normalmente sono pezzi unici e preziosi che richiedono nuove metodologie analitiche non invasive. Sebbene alcune delle problematiche trattate derivino dal particolare approccio adoperato, queste possono essere considerate come tematiche generali che riguardano la tecnica di spettroscopia ad immagine, che è ancora nelle prime fasi di sviluppo in quest'area. Per questo motivo, il presente lavoro può essere considerato di grande interesse per la comunità scientifica che si occupa delle problematiche riguardanti i beni culturali.

La tecnica di spettroscopia ad immagine può essere vista come l'estensione in due dimensioni della spettroscopia puntuale UV-VIS-NIR. Le informazioni ottenute possono essere impiegate per caratterizzare, mappare e monitorare materiali che costituiscono i beni culturali. Si tratta di una tecnica non invasiva che permette di avere anche dispositivi portatili. Se si considera il tipo di informazioni raccolte con questi sistemi di misura, senza contatti né operazioni di campionamento, appare ovvio che la tecnica possa essere un potente strumento analitico nel campo dei beni culturali. Il dispositivo sviluppato permette l'acquisizione di spettri in riflettanza diffusa di vaste superfici (fino a 3 metri di larghezza). I dati raccolti possono essere usati nella caratterizzazione, mappatura e monitoraggio di materiali che costituiscono questo tipo di manufatti.

La parte centrale di questo lavoro di dottorato si focalizza sulla messa a punto di una metodologia di misura per acquisire spettri in riflettanza diffusa tramite la spettroscopia ad immagine. Per realizzare questa operazione, diversi campioni sono stati studiati, inclusi alcuni preparati *ad hoc*. Alcune prove sperimentali hanno permesso di identificare problematiche nella metodologia

sviluppata, ma sono stati risolti con esito positivo. Alcune repliche di laboratorio sono state preparate in forma di film pittorici che successivamente sono stati esposti a un processo d'invecchiamento accelerato ripetute più volte. Nel corso di questo procedimento, i campioni preparati sono stati monitorati mediante il sistema di spettroscopia ad immagine, che è stato in grado di seguire i cambiamenti nelle proprietà ottiche di queste repliche. I risultati mostrano che la metodologia di misura sviluppata per acquisire spettri in riflettanza diffusa nell'intervallo da 420nm fino a 850nm può presentarsi come un potente strumento analitico che permette la caratterizzazione, differenziazione, mappatura e monitoraggio di materiali usati nei film pittorici (ad esempio i pigmenti). Un procedimento simile è stato adoperato per mettere a punto una metodologia di misura mediante spettroscopia ad immagine per raccogliere spettri in trasmittanza nello stesso intervallo di lunghezze d'onda. Il proposito di questa operazione è applicare le misure effettuate in questa modalità allo studio di cromofori di oggetti vetrosi riguardanti i beni culturali come le vetrate artistiche.

Ambedue i metodi di misura sono stati applicati per indagini di manufatti artistici con l'obbiettivo di dimostrare le potenzialità delle procedure per risolvere problemi analitici che riguardano l'ambito dei beni culturali. La metodologia in riflettanza è stata applicata *in situ* per lo studio interdisciplinare di un dipinto murale nel corso di un'operazione di restauro. I risultati hanno permesso l'identificazione della maggior parte dei pigmenti impiegati per realizzare l'opera, di alcuni materiali utilizzati nell'intervento di restauro e hanno mostrato i vantaggi di un approccio multi-tecnica, non invasivo ed effettuato con dispositivi trasportabili, accoppiando la spettroscopia ad immagine alla tecnica di fluorescenza X. Le analisi in trasmittanza sono state realizzate simultaneamente su un gran numero di tessere vetrose colorate di una vetrata artistica. Gli spettri raccolti hanno permesso l'identificazione di vari cromofori nei campioni studiati.

Dai risultati ottenuti si può affermare che la spettroscopia ad immagine si mostra come una tecnica interessante e ancora non completamente sfruttata per lo studio di materiali riguardanti gli oggetti del campo dei beni culturali. Nell'intervallo del visibile, la principale applicazione sembra la caratterizzazione, differenziazione, mappatura e monitoraggio di pigmenti in dipinti, manoscritti, etc. Comunque, grazie alla sua grande versatilità, questa tecnica si è dimostrata anche un potente strumento per l'analisi dei cromofori impiegati nei manufatti vetrosi.

A mis padres y hermanos
Para toda mi familia
Para mi cuadrilla
Para Ti

NUÑO.– ¡Qué cosas se ven, don Pero!
PERO.– ¡Qué cosas se ven, don Nuño!

La venganza de don Mendo, PEDRO MUÑOZ SECA

Vaben….Doman..

Contents

Chapter III : The Imaging spectroscopy system 75

Introduction

Chemistry is the science concerning the composition, structure, and properties of matter, as well as the changes that undergoes during chemical reactions. Different branches of this science such as organic, inorganic, analytical or environmental chemistry play an essential role on the applicative field regarding cultural heritage preservation. Most people thinks of cultural heritage in terms of monuments, buildings, art galleries or museums but this approach does not take into account the key role who play sciences as chemistry in the conservation, restoration and prevention practice of this interdisciplinary field. Chemistry for cultural heritage is required when dealing with this kind of objects in terms of diagnosis, state of conservation, production techniques of ancient materials and artefacts, development of restoration tools and methods, prevention of undesirable changes, organization, management and execution of restoration-conservation-prevention procedures and in the monitoring process for the detection of any kind of deterioration. There are several important motivations to preserve art and archaeological objects: economical, historical and/or sentimental, aesthetical. For these reasons, is essential that scientists use their knowledge and specific skills to reach this goal.

When studying cultural heritage objects, numerous problems have to be faced and careful attention must be taken. Complementary methodologies are from different experts are required: physicists, chemists, archaeologists, art historians, engineers, restorers, curators… had to work together adopting an interdisciplinary approach. This mode to face the study of cultural heritage objects is not easy because it needs a large number of expertise working together. Moreover, these specialists have different points of view and the requirements of one approach could be opposed with the requests of the others. Despite these difficulties, this kind of interdisciplinary methodologies are adopted most frequently when dealing with preservation of cultural heritage objects. In this context, the present work focuses on the field of Chemistry for Cultural Heritage, but it has been developed with a close and continuous collaboration with experts of the engineering, handicraft, restoration and art history areas in order to reach the maximum fruition.

Diagnosis is one of the crucial phases in studies concerning works of art and archaeological artefacts: knowing as much as possible about the materials constituting cultural heritage objects is fundamental for their preservation. The composition of the materials employed in the past are used to date objects, to identify the degradation processes that affect their integrity, to detect forgeries and retouches or to decide which product is most convenient for a restoration process to prevent incompatibilities or undesirable effects between former and intervention materials. If diagnosis is realized at different times in order to develop various action plans (prevention-restoration-conservation) with as much knowledge of the situation as possible, then the diagnostic becomes monitoring which is an indispensable operation for an adequate maintenance. Analysis at the atomic, molecular or supramolecular level of cultural heritage objects presents difficulties arising from the particular features of these samples: they are precious and sometimes unique pieces. For this reason one of the indispensable tasks of this interdisciplinary field is to propose novel non-invasive methodologies. Although there is a wide variety of analytical techniques, the choice between them depends greatly on the type of information required and on the characteristics of the sampling procedure. This operation is one of the most delicate of the analytical approach, but in this case it is even more critical due to particular nature of the samples under consideration. Analytical techniques can be classified from this point of view in different groups: non-invasive (non-destructive, without sampling and contact), non-destructive, micro-destructive or destructive techniques. Obviously, in order to characterize the materials of the art objects the non-invasive and if it is possible transportable techniques are favoured. However, cultural heritage is a complicated area where samples are complexes systems and the required information is sometimes difficult to reach, even using invasive analytical techniques. Depending on the characteristics of the case under study, different problems need to be tackled and a thorough diagnostic project must be designed considering the information expected, the sampling procedure required and the available resources. Taking into account these considerations, a multi-technique approach is suitable if the potentialities and limits of such instruments are known and it is possible to obtain complementary information [1,2].

In recent years, the acquisition of multispectral or hyperspectral images of art objects as paintings has become rather popular in the researching community dealing with cultural heritage applications due to the capacity of such techniques to obtain a large amount of information overcoming all the limitations and problems involved in sampling operations. Imaging spectroscopy (IS) extends the measurement domain of one-dimensional UV-Vis-NIR spectroscopy to the two-dimensional domain providing information which can be used to characterize, to map and to monitor materials constituting works of art. Basically, it consists in the recording of a set of two-dimensional monochromatic images within a range of wavelengths [1-7]. This technique has different applications. The obtained data can be used for archiving, dissemination or documentation purposes and also for virtual restoration of works of art [3,6]. However, imaging spectroscopy provides not only the digital reconstruction of the surface under concern. The acquired images are handy interfaces to study the spectral information of the regions of interest. Within the visible range, this allows to achieve high color fidelity: acquiring the spectral reflectance is the most reliable way to reproduce colours faithfully, where faithfulness is measured in terms of independence from illumination and acquisition devices. Moreover, from the recorded spectra, it is possible to obtain information about the materials constituting the cultural heritage objects. The reliability of the spectral analysis clearly depends on the accuracy of the its reconstruction, which in turn is determined by several factors, such as the instrument's spectral resolution, the measurement noise, the choice of the illumination source or the wavelength range under consideration. Imaging Spectroscopy is a non-invasive technique and the developed measuring devices can be transportable. Considering the type of information acquired by this kind of system without sampling and contact, it seems obvious that this technique can represent a powerful tool for the cultural heritage field. Nevertheless, hyperspectral and multispectral imaging still present different problems and poses technical challenges that need to be discussed and examined.

The aim of this doctoral thesis is to study the application of imaging spectroscopy on the field of chemistry for cultural heritage. In particular, the Laboratory for Ultraviolet and X-ray Optical Research (LUXOR) which is a structure afferent the Institute for Photonics and Nanotechnologies (IFN) of the *Consiglio Nazionale delle Ricerche* (CNR) has developed in collaboration with the department of Information Engineering (DEI) of the University of Padua a transportable imaging spectroscopy device. Basically, it consists on a visible imaging spectrograph (which can be considered as the core of the IS acquisition device) mounted on a rotation stage. The spectrograph consists of three main optical components: the objective, the dispersing element and the CCD camera. The system has been built to study even large-sized surfaces such as those found in frescoed halls [8, 9]. In the present work, the potentialities of such kind of systems for the study of works of art and archaeological artefacts, mainly focusing on the applications on the chemistry for the cultural heritage field will be examined and discussed.

The imaging spectroscopy device is in order to acquire visible diffuse reflectance spectra of entire large-sized surfaces (up to 3m wide). The collected data can be used to characterize, map and monitor materials constituting cultural heritage objects, as pigments in paintings. However, to understand and elucidate the obtained information can be difficult, because the samples under consideration of this peculiar field are very complex mixtures. The absorption bands are generally broad, they may be shifted few nanometres or reduced in intensity and in some cases not sufficiently characteristics. In addition, particle size and the presence of other components on the heterogeneous samples as binders or varnishes cause different optical effects as yellowing. Nevertheless, diffuse reflectance spectra can often permit the differentiation of materials of cultural heritage objects, as pigments or inks even with similar hues, by examining the absorption band profile and contour (specially under the skilled eyes of a scientist). In fact, there are several works in bibliography where diffuse reflectance spectra (obtained with "spot" techniques as FORS, Fiber Optics Reflectance Spectroscopy) in the ultraviolet/visible/near-infrared (UV-Vis-NIR) range had been applied to the study of dyes and lakes [10,11], of pigments in manuscripts [12] or in mural paintings [13-15], of colouring agents in paintings [16,17], of painting mixtures [18] or of chromophores in glassy objects [19,20]. All of them show the advantages of the reflectance spectroscopy to study *in situ* materials concerning cultural heritage objects in a non invasive way, specially when it is integrated with other techniques in order to obtain complementary information of the object under consideration. Even if UV, Vis, and NIR reflectance are widely accepted by the scientific community, they are so far limited applied in spite of its ability in the diagnostic of works of art and archaeological artefacts, without the need of sampling [14].

Imaging spectroscopy obtains diffuse reflectance spectra as a function of the localization in the investigated surface, thus mapping the samples which is a really useful feature when dealing with such heterogeneous objects as those of the cultural heritage field. For monitoring purposes, this capacity is essential because with "spot" techniques it can be difficult to acquire the analysis exactly in the same position (repositioning) at different times. However, the spectra recorded have an inferior spectral resolution in comparison with "spot" techniques and generally a narrower wavelength range, giving spectral data that in some cases could have less power resolution for the characterization of art materials. Despite the potentialities of the technique, it has not been frequently used for the study of works of art and archaeological artefacts. The technique is gaining importance but the applications of reflectance imaging spectroscopy is mainly focused on the study of pigments in paintings or palimpsests [21-23].

Taking into account these considerations, imaging spectroscopy appears as an interesting and not fully exploited technique to study materials concerning cultural heritage objects. In the visible range, the principal application area seems to be the characterization and/or differentiation, mapping and monitoring of colouring agents in paintings, manuscripts...but not only, because it could be helpful in the identification of chromophores of glassy objects as instance.

In the present doctoral dissertation, these aspects regarding imaging spectroscopy will be analysed and discussed. This research project has progressed in different phases. As a starting point, in collaboration with the LUXOR laboratory (Dr. Poletto and Ing. Ratti) and of the DEI (prof. Cortelazzo), a measurement methodology with the imaging spectroscopy system developed has been optimized. For this purpose, several tests have been performed on laboratory and real samples with a known visible reflectance spectra. In this way, technical problems and factors that could be improved have been individuated and then optimized in order to obtain the best results from the spectroscopic point of view. In this context, the main issues that would be examined and discussed are the experimental setup, the spectral and spatial resolution, the wavelength range, the calibration or the signal to noise ratio. Then, additional experiments have been performed on laboratory samples artificially aged to verify the ability of the optimized methodology to observe changes on the optical properties of simple systems. In this procedure, the analytical power of the system to characterize, differentiate, map and monitor pigments has been tested in order to comprehend its potentialities and limits.

Subsequently, the developed measurement system has been tested on real artefacts. In particular, a study on a mural painting has been performed. The aim was to understand the validity of the imaging spectroscopy device to characterize and to map the pigments used to elaborate the work of art and the advantages when it is used with a complementary non-invasive technique, in particular with portable micro X-ray Fluorescence (µ-XRF). The analysis has been executed during a restoration process. The intervention was conducted following a multidisciplinary methodology: art historians, restorers, scientist and engineers have worked together. Several issues have arisen throughout the restoration and faced with a continuous and stimulating dialog between the different approaches. The case study must show the potentialities and limits of the non-invasive analysis conducted through the transportable µ-XRF and imaging spectroscopy devices to solve such issues as the author's palette or the execution period. The discussion would emphasize the role and contribution of imaging spectroscopy in this methodology.

The imaging spectroscopy device was conceived to acquired reflectance spectra in the visible. Anyhow, if the objects studied are transparent the system is versatile and can be adapted to perform transmission measurements. Glass is a transparent material widely used from the antiquity times up to nowadays in order to elaborate work of arts or different artefacts as mosaics, stained glass window or jewellery. UV-Vis-NIR spectroscopy is largely employed for the study of colouring agents in coloured glasses [19, 20, 24].

If the vitreous objects are wide, imaging spectroscopy can represent a powerful tool to characterize and to map chromophores in large-sized surfaces. When studying opaque objects as mosaic tesserae, the reflectance mode is the only measurement modality that could be adopted. In fact, this is an application were imaging spectroscopy may be a valuable analytical technique. On the other hand, when dealing with transparent objects as glass bottles, cups or stained glass windows both modalities, transmittance and reflectance, could be applied. For this reason, a measurement methodology in transmittance mode has been also settled. To comprehend the validity of the developed setup, various tests have been performed on coloured glasses comparing the results obtained with the imaging spectroscopy device with the ones given by a laboratory spectrophotometer.

Then, the system measurement developed has been applied to the study of stained glass windows. These works of art are really complex and heterogeneous objects composed, together with other materials, of numerous coloured glass tesserae that can be decorated with grisailles (coloured layers applied on the glass surface in order to elaborate designs, lines and shadows). In fact they can be described as "paintings of light". Taking into account the characteristics of this kind of samples, the analysis through imaging spectroscopy in the visible range seems a challenge and an interesting application. For these reasons, the opportunity has been taken when the occasion has risen throughout this research project. As in the case study on a mural painting, the aim of these measurements is to understand the potentialities of the imaging system to characterize and to map colouring agents, in this case chromophores in vitreous objects. The assets of a multi-technique approach with portable µ-XRF will be examined and discussed.

The general purpose of this work is to present the results in a critical and analytical way, in order to validate the role that imaging spectroscopy device can have on the field of chemistry for cultural heritage. The advantages of integrating different analytical non-invasive techniques must be faced too, because it seems obvious that most of techniques need to be integrated by complementary experimental approaches. Furthermore, dealing with the particular area of cultural heritage field it is necessary to consider the contribution of an interdisciplinary approach, in order to reach the maximum fruition. This research project is the result, as it was said before, of years of collaboration with engineers, art historians, restorers and artisans. Sometimes, the interaction with these different expertises has been difficult but the end result worth final result is worthwhile to all the efforts made in this direction. Lastly, it must be said that in this interdisciplinary approach the key role of the chemist is demonstrated. This science is essential in order to understand different phenomena concerning cultural heritage issues.

The present doctoral dissertation is structured in the following chapters:

- **Chapter I:** Presentation and State of art of Imaging Spectroscopy technique. Application fields and principal utilities on the cultural heritage area. Comparison with some techniques used in this area. Multi-method approach: advantages, complementary information and analytical skills of non-invasive transportable “laboratories”.

- **Chapter II:** Description of some materials of interest of the cultural heritage field. Basic Structure of paintings. Main painting materials. The paint layer. Colourants. Some mechanism of production of colour. Main incompatibilities and alteration processes. Mural paintings. Glass, some generalities. Short history of glass and some vitreous art materials.

- **Chapter III:** Imaging Spectroscopy system and measurement methodology. First tests. Optimization of the acquisition setup: illumination system, calibration, wavelength range and resolution, signal to noise, spatial resolution. Improvement of different parameters using tests on different laboratory samples including some experiments dealing with artificial ageing process. Comparison with spectrophotometer results. Measurement setup in transmittance mode to analyse wide glassy objects, comparison with spectrophotometer data.

- **Chapter IV:** Application of the developed measurement system to the study of mural paintings. Realization of laboratory replicas to be used as references. Case Study: mural painting of “Santa Caterina”. Interdisciplinary approach to the piece of work. Description of the work of art. Diagnosis phase preliminary to the retouching stage. Second campaign of analysis. Utility of the data provided by the imaging spectroscopy technique and from a multi-technique approach: Integration with XRF data. Results and conclusions.

- **Chapter V:** Application of the developed measurement system to the study of glassy objects.: case study on the stained glass windows from the Scrovegni Chapel of Padua. Potentiality of the transmittance mode and “double-transmission” modality as a solution when transmittance measurement is not possible. Validity and utility of imaging spectroscopy data. Advantages in a multi-technique approach integrating IS with XRF technique, Results and conclusions.

Chapter I : Imaging Spectroscopy

Imaging Spectroscopy (IS) has been developed by combining digital imaging and spectroscopy. The technique is based on irradiating the surface under study with broadband continuous sources, such as halogen lamps, and detecting, with a suitable device, the back-scattered, transmitted or emitted radiation within narrow spectral ranges. Each image collected in the series represents as instance the reflectance of the object under study for optical wavelengths within a narrow spectral range. Until recently, images obtained with this kind of devices were restricted to a few broad wavelength bands by the limitations of detector designs and the requirements of data storage, transmission and processing. Recent advances in these areas have allowed the design of hyperspectral imaging systems that have spectral ranges and resolutions comparable to ground-based spectrometers. Known as multispectral or hyperspectral imaging spectroscopy, depending on the number of wavelength bands, in this technique multiple channels are used to capture the signal across the spectral range. This technique has already been applied in other fields as astronomy or medical sciences [25]. Imaging spectroscopy is a non-destructive, portable and, relatively fast and economical technique that can represent a powerful tool for the study of artworks.

In this chapter, some main issues regarding imaging spectroscopy will be presented and discussed. Firstly, the technique will be described, examining some theoretical and technical principles including some basic concepts of reflectance spectroscopy and colourimetry. Then, the state of the art of imaging spectroscopy will be withdrawn, taking particular attention to its use in the study of artistic and historic objects . At that point, the technique will be compared with some techniques used in this specific area taking into account its characteristics, advantages and disadvantages when dealing with artworks. Finally, it will be considered its participation on a multi-method approach and its possibilities on a non-invasive transportable laboratories.

I.A Principles of Imaging Spectroscopy

With the advances in computer and detector technology, the new field of imaging spectroscopy is developing. This is a new technique for obtaining a spectrum in each position of a large array of spatial positions so that any spectral wavelength can be used to make recognizable images. The image might be of a paint in laboratory or a whole planet from a spacecraft or Earth-based telescope [26].

Some analytical methods rely on exhausting preparative operations in order to obtain homogeneous solution containing the analyte of interest from the sample. However, in numerous cases as in the industry or biological field many processes depend on heterogeneous environments or mixtures. A more complex analysis is required in order to understand these analytical problems. This goal can be reach by mapping these systems in two, three or even more dimensions. Visualization using images has always been an integral part of scientific work and its use is constantly increasing. The availability of electronics and computing has improved the use of mapping of heterogeneous systems. Imaging can be microscopic, if a charge-coupled device (CCD) camera is put on top of a microscope as in electron microscopy, or macroscopic as in satellite or airborne imaging. Generally speaking a multivariate/hyperspectral image is an image where each pixel is represented not by one gray value, but by a vector of gray values. They are a group of gray level images one for each variable. In many cases the vectors are spectra. Different variable types can be used to produce these 2-D and 3-D multivariate/hyperspectral images. The image of the object can be acquired over time or in different variable, e.g. wavelength. In this context, multivariate and hyperspectral image analysis is a methodology of analysis that gather an elevate number of different techniques as secondary ion mass spectrometry (SIMS) imaging [27].

The term *imaging or image spectroscopy* (IS) usually is taken to mean the recording of a set of two-dimensional images of a certain object at different wavelengths within a given spectral range [1]. It can be seen as the two-dimensional extension of the punctual spectroscopy. Spatial and spectral information is simultaneously recorded: light intensity is registered as a function of both location (pixel in the image) and wavelength. In the imaging field, the data set includes a complete digital image of the sample under consideration at each wavelength over the entire spectral interval. On the other hand, in the spectroscopic domain, a diffuse reflectance, fluorescence, or transmittance (it depends on the measurement modality) spectrum is obtained for every single point (pixel on the digital reconstruction of the image that represent the studied surface of the sample under consideration). The acquisition of a sequence of digital images at intervals trough a wavelength range has as result a three dimensional image cube which is known as Spectroscopic image data cube or Hypercube or Hyperspectral/Multispectral image [21, 22, 27-31]. Figure 1 (on next page) shows a representation of the data set collected by imaging spectroscopy (i.e., hyperspectral image).

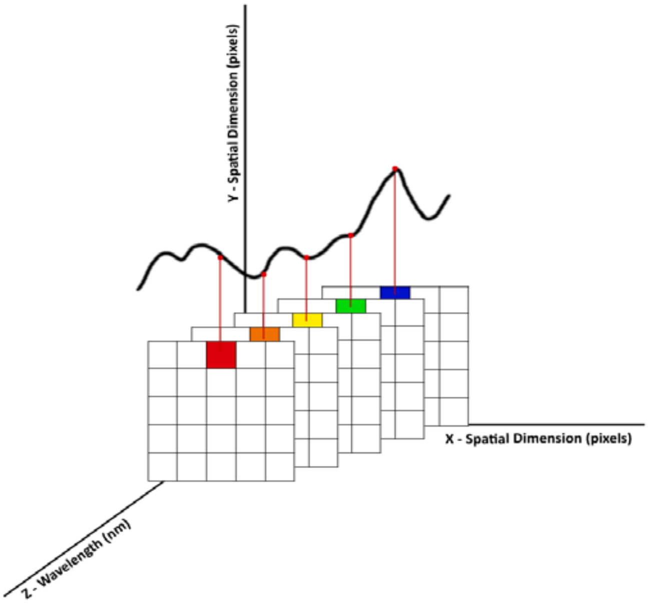


Figure I.1- Spectroscopic image data cube or Hyperspectral/Multispectral image

As it is shown on Figure I.1, a hyperspectral/multispectral image is a multilayer data set formed by a stack of images. The sheets through the data cube, defined by the spatial (pixel) dimensions X and Y represents the collection of images taken at individual optical wavelengths, and the Z dimension represents the wavelength. The data obtained by pursuing the Z dimension of the hypercube at any pixel correspond to the spectral information for that particular point of the sample studied. The wavelength bands are usually equally spaced within the considered region of the electromagnetic radiation, near-infrared (NIR) as instance, so a full spectrum through this frequencies range can be obtained for each pixel (NIR-spectrum for example).

The difference between multispectral and hyperspectral images is determined by the magnitude of the set of data, in particular by the number of images collected at different wavelengths. Traditionally, the number of wavelength bands was usually less than twenty [32] or ten [33] and the term was multispectral image. Further developments in this field gave rise to the possibility to acquire much larger number of wavelength bands and the term used, inherited from the remote sensing area, is Hyperspectral image [32,33]. From another point of view, justified once more from the historical development of the technique on the remote sensing field, some authors intend multispectral imaging as the collection in very far portions of the electromagnetic spectrum, X-ray and infrared as instance. Instead, hyperspectral imaging contains a sequence of images in an homogeneous spectral range [34].

The wavelength intervals within it is possible to operate cover from the ultraviolet (UV), the visible (VIS) up to the infrared (IR) region. Hyperspectral imaging is used today as a conjunction of digital imaging with a variety of spectroscopic techniques. The analysis modality can be acquired in diffuse reflectance, absorbance or in fluorescence mode [21, 29, 31, 32, 34-36].

As it has been outlined previously, in this doctoral dissertation the application to the chemistry for cultural heritage of diffuse reflectance imaging spectroscopy in the visible range will be discussed. Reflectance modality has the principal advantage to be a non-invasive approach to study translucent or opaque solids, as many cultural heritage objects like paintings. This characteristic makes reflectance modality of great interest for the study of works of art. On the next section, some basic concepts of reflectance spectroscopy will be presented briefly. This information must be kept in mind to a better understanding of this research work.

I.B Some topics regarding Reflectance Spectroscopy

Diffuse reflectance imaging spectroscopy records the light as a function of wavelength that has been reflected or scattered by media composed of discrete particles across a determinate region of the electromagnetic spectrum, as the visible range in the particular case of this doctoral dissertation. Most of *surfaces* consists of particulate materials, in some cases particles are disperse, as in clouds, or embedded in a transparent matrix, as in paintings, or fused as in ceramic or glassy objects. The point is that analysing reflectance spectra of an object it is possible to extract information from its scattering properties [25, 26, 35].

The terms *reflectance* and *reflectivity* both refer to the fraction of incident light scattered or reflected by a material. Although they are sometimes used interchangeably, reflectance has the connotation of the diffuse scattering of light into many directions by an uneven surface (diffuse reflectance), whereas reflectivity refers to the specular reflection of radiation by a smooth layer (specular reflection). Electromagnetic radiation interacts selectively with matter by inducing different transitions between two energy levels of atoms, molecules or ions constituting a material. The absorbed radiation has a frequency corresponding to the energy gap between the two levels, in this way an absorption spectrum provides information about the composition of matter. Reflectance spectroscopy is a powerful technique for measuring the characteristic absorption spectrum of a material. This can be done by the inversion of the reflectance, in order to determine the spectral absorption coefficient of the material or, at least, some quantity proportional to it. There are some advantages when using this measurement modality. Firstly, multiple scattering amplifies the contrast within very weak absorption bands in the light transmitted through the particles, while very strong bands can be detected by anomalous dispersion of the radiation reflected from the particle surfaces. One of the principal benefits of this measurement mode is the no requirement of sample preparation, which is essential for the field of chemistry for cultural heritage. Indeed, except for a few exceptions such as glass objects or stained glass windows, works of art are opaque. There are some drawbacks when this measurement modality is adopted, especially when real artworks are considered. As it has been mentioned before, cultural heritage objects are usually heterogeneous complex systems. In these cases, numerous disturbing effects have to be taken into account as the variations in the size of particles (as pigments in painting films), the possible colour fading or the presence in the sample of interference components as varnishes or binding media. All these factors affect absorption and scattering properties and the reflectance spectrum can be very complex and difficult to rationalize [1, 18, 37].

Scattering is the process that makes reflectance possible. The optical path of photons is a random walk: photons enter a surface and suffer different processes as absorption or scattering. Interaction between the electromagnetic radiation and a partly transparent media is governed by a combination of reflection, absorption, scattering and emission processes, depending on different parameters as the geometry, the refractive index, the roughness of the surface, the characteristics of the light…. In Figure I.2 it is shown the possible interactions concerning a beam of light and a partly transparent media. The incident beam is partly reflected, as it can be observed on the scheme in Figure I.2. Some of the reflection occurs in a “mirrorlike” or specular reflection (reflectivity, governed with the law of equal angle of reflection equal to the angle of incidence).

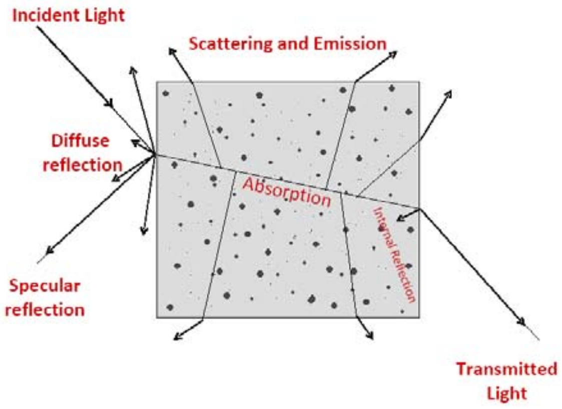


Figure I.2- Effects suffer by a beam of light passing through partly transparent medium

The other part is the diffuse reflected light scattered randomly from the surface (reflectance). The balance between specular and diffuse reflection depends on how smooth or mat is the surface. Diffuse reflectance originates from a more intimate interaction with the object than specular reflection does and reveals the colour of the medium. Apart from attenuated total reflection (ATR) techniques used, as instance in infrared spectroscopy, reflectance spectroscopy is concerned with diffuse reflection, so instruments are built in order to avoid the collection of specular reflectivity. The diffuse reflected light carries information on the composition of the material, since the electromagnetic radiation enters up to some extent in the medium. The penetration depth of the light depends on its wavelength. As an example, since most pigments are transparent to NIR wavelengths, infrared reflectography is used even to study the ground layers of a painting, while visible radiation does not penetrate so far and is useful to study the upper coloured layers. If the surface is extremely irregular, light is almost completely scattered at the multiple interfaces with slight penetration and little coloration is perceived. The portion of the radiation which is not reflected at the medium surface enters into the substance as it can be seen in Figure I.2. Part of the light can be absorbed and other may be scattered inside the material. For example, if the medium is composed of pigment grains dispersed in a binding media, when light encounter a particle a certain percentage is absorbed. If the grains are dark the major part of light is absorbed while, if particles are bright, scattering is the most common process, and the light continues its random path. This process justified the enhancement of weak features in reflectance spectroscopy. The amount of light scattered and absorbed depends also on the particles size: a larger dimension produces more radiation absorption because of its longest internal path while smaller elements gives more reflection. As it can be seen in Figure I.2, light proceeds its path inside the medium and when it arrives to the other interface it can be internally reflected. The absorbed radiation may be converted into heat (non radiative process) while in other cases it may be reemitted as fluorescence as instance. Lastly the residual beam of light exits the medium with a deflection of some degree due to the difference between the refractive indexes of the air and of the medium under consideration [1, 25, 26, 37, 38].

I.C Colourimetry

Colour is an essential characteristic of any cultural heritage object. When an artist or craftsman realizes a piece of work, the choices that he makes in terms of "colour" as tone, saturation, hue, shade or textures are an important and personal decision and they must be respected. For this reason, colourimetry is a significant discipline when dealing with the cultural heritage field.

Colourimetry deals with the objective description of the physical correlates of colour perception [39]. It is not trivial to define the term "colour" since it depends on physical and psychological factors. Its perception is intrinsically correlated to the observer, the surrounding conditions, the illumination… Light sensation is produced by the visible range, falling within the wavelength limits of 380 nm and 780 nm. Radiation from the short wavelength region of this radiation produces usually the sensation of blue light, radiation with wavelengths between 520 nm and 550 nm are seen as green light, and above about 650 nm we perceive the light usually to be of red colour. These limits are not well defined, and the actual perception depends strongly on the adaptation state of the eye and on light stimuli surrounding the test object. There are two fundamental methods of producing colour stimuli: additive and subtractive colour mixing. In additive colour mixing lights are mixed, as in colour TV displays. Instead, in subtractive colour mixing, colorants remove some part of the visible spectrum. The description of opaque colours can be realized by comparison with collections of painted chips or based on the Commission International de l'Eclairage (CIE) system. CIE conventions conclude that to quantitatively describe colour there are three tristimulus relevant values: hue (wavelength), saturation (purity) and luminosity (intensity of reflected light). These elements are assigned by X, Y, and Z, respectively and they are obtained by the measurement of the object reflectance and source emission spectra. Y corresponds to the perceived luminosity of the light source, while X and Z provide the chromaticity of the spectrum.

The most widely used method to define colour and to describe colour changes is the CIELAB 1976 system that starts with the tristimulus values X, Y and Z and then defines other three coordinates *L*, a*, b**. *L** represents the lightness (*L** = 0 yields black and *L** = 100 indicates diffuse white), *a** the position between the magenta-green (-128= green, +127=magenta) and b* its position between Yellow-Blue (-128=blue, +127=yellow). CIE *L*a*b** chromatic coordinates provide a definition of the colour. Using this colour space, it is possible to calculate the difference between the colour of two different samples or of the same object at two different times. The vector E_1 (L_1*, a_1*, b_1*) and the vector E_2 (L_2*, a_2*, b_2*) correspond to the chromatic coordinates of the samples 1 and 2 respectively. Colour difference is provided by the modulus of the difference vector:

$$\Delta E= E_2-E_1= [(\Delta\, a^*)^2 + (\Delta\, b^*)^2 + (\Delta\, L^*)^2]^{1/2}$$

It is considered that human eye is able to detect colour changes such as $\Delta E \geq 1$. Since the *L*a*b** model is a three-dimensional model, it can only be represented properly in a three-dimensional space. However depictions can be obtained by realizing sections with a fixed lightness. These two-dimensional CIE Lab diagrams allow the plotting of colour in function of X, Y and wavelength, as the example in Figure I.3. The horseshoe-shaped curved line covers the visible wavelengths from violet at 380nm to red at 700nm and it is known as *spectrum locus* [1, 25, 38, 39].

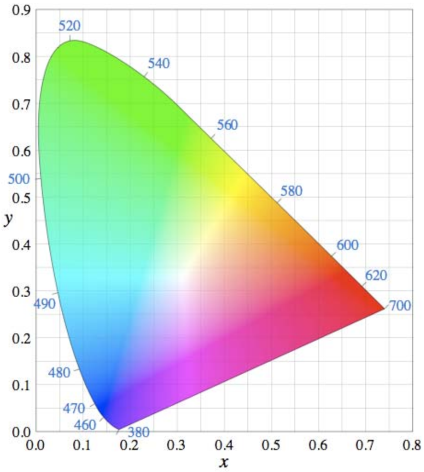


Figure I.3- Two-dimensional chromacity diagram

In order to obtain the CIE *L*a*b** chromatic coordinates it is necessary to analyse the object under consideration. These measurements can be done with a tristimulus colourimeter that is fast, handy and inexpensive. However, the acquisition of the spectral reflectance in the visible range is the most reliable way to reproduce colours faithfully, where faithfulness is measured in terms of independence from illumination and acquisition devices. Therefore reflectance imaging spectroscopy in the visible region can be used to obtain information about the composition of cultural heritage objects through an elaborate interpretation of the reflectance spectra and from them it is possible to calculate the CIE *L*a*b** chromatic coordinates. This doctoral dissertation focuses mainly on the extraction of chemical information from the visible spectra obtained. Nevertheless, measurement of the colour is important in cultural heritage field for manufacturers as in the elaboration of pigments or protective products or for users as the restorers and this represent an important application of this technique.

I.D State of the art of Imaging Spectroscopy

Imaging spectroscopy is an analytical technique developed principally in the remote-sensing world, although now is progressively being used in a wide variety of unrelated areas. Moreover its employ is growing due to the numerous advantages presented by the technique [35].

Airborne imaging from balloons and airplanes on black and white colour and infrared films is a very old technique. The launch of the first weather satellite during the sixties, had as a consequence, that satellite imaging has increased the mapping of heterogeneous systems and then it has evolved rapidly. However, the major application was to explore the spatial information to one gray level image. Subsequently, scientist realize that it was possible to obtain spectral information acquiring data set with various layers of gray level images. Advances of different areas concerning the technique (detectors, data storage, processing..) led to different improvements as the application in more than one wavelength band. In fact, imaging spectroscopy must be enhanced and explored from both the spatial and the spectral point of view. At the late eighties multivariate satellite and airborne imaging has been called *Hyperspectral* imaging. The gathered data can be used in geology, agriculture, archaeology, hydrology, climate studies, etc. In some cases it is even possible to realize chemical analysis from the distance as the detection of minerals [27]. From the remote sensing area, imaging spectroscopy was then applied in other fields as in medical applications for instance. The possibility to obtain spectral and spatial information at the same time and to produce images of the acquisition scene in a non-destructive way and without contact make imaging spectroscopy really interesting for a broad number of application areas. On the medical field, it can represent an improvement for example in the visualisation of abnormal morphological features for a better diagnosis. The biological area is normally characterized by delicate and heterogeneous samples where processes can be studied and monitored in time using IS technique. The implementation of the design and construction of the imaging spectroscopy devices allows, in addition, the location of these systems in the processing chains of many industrial sectors in order to realize quality-control procedure as instance. In fact, there are some references regarding the application of imaging spectroscopy to the study of other fields as in geology [26], in medicine [27, 40], in forensic science [31, 41], in industrial applications [42, 43], in food processing [44] or control [45] or in biological studies [46, 47].

Taking into consideration the application of imaging spectroscopy to the study of works of art, the first attempt from an historical point of view can be considered a series of studies on different paintings realized at the National Gallery in London in the thirties. A visual colorimeter was used to measure the three values of the primary colours in order to detect chromatic changes in these art objects. Subsequently, a rough broad-band imaging spectroscopy was performed by photographing the artworks after inserting RGB (Red, Green, Blue) filters in front of the lens of the camera. A further progress has been reached using an IR false colour film. The emulsion of the film is constituted by three layers sensitive to the green, red and IR regions of the electromagnetic spectrum and finally a suitable filter gets rid of the blue light that affects the three layers. The photographic method is quite limitative, so since the eighties it has been more and more frequently replaced by solid-state television (TV) cameras connected with computers in order to store and recover images. In 1988, once more at the National Gallery of London, a prototype was built that worked in the VIS range using three standard colour separation filters. During this study, the researchers suggested the possibility to use a set of narrow-band interference filters and the expansion to the NIR range. Afterwards, this idea was developed and applied to actual cases where mainly two approaches were followed: to illuminate with monochromatic light the artworks or the use of a set of narrow filter or a dispersive element in front of the video-camera lens [1].

In 1989, a European Community-supported project called VASARI (Visual art systems for archiving and retrieval of images) initiate with the aim to replace the technical photography of paintings. The result of this project was the development of two imaging systems, one installed at the

National Gallery of London and the other at the Doerner Institute of Munich. With a further European initiative, MUSA European Project 7523, a third system was installed at the Galleria degli Uffizi in Florence. From 1993 to 1996, the European Community-supported for art reproduction in colour (MARC) project applied VASARI to the printing of high quality art books [3]. The multispectral imaging system VASARI provided seven bands in the visible range (400 to 700nm) producing extremely accurate colorimetric images of paintings of the National Gallery of London. The system succeeds in monitoring colours of this kind of artworks but multispectral data could not be used to obtain reflectance spectra on a per pixel basis. In order to improve the spectral information, the National Gallery research group participate on another European Union funded project. CRISATEL has developed a multispectral camera with a very high spatial resolution. It consisted on a imaging system using a CCD camera as a sensor mounted on an X-Y scanning stage and has a wavelength range from 400 to 1000nm using thirteen interference filters in front of the camera lenses. This device allows the identification of certain pigments through the reflectance spectral reconstructed [48]. Subsequently, multispectral imaging systems have been developed and applied to the study of paintings by several research teams as it can be seen in different references [4, 7, 36, 49-51]. This kind of devices has been applied to study some masterpieces as the Van Gogh's Self-portrait at the National Gallery of Art of Washington D. C. [52] or the *Mona Lisa*, which is considered the most famous painting of the world [6, 53-55]. These works show some of the potentialities and possible applications of imaging spectroscopy in the cultural heritage field. However, spectral information in these researches seems to be not completely exploited in spite of other potential applications as digital archiving or colourimetry measurements. It can be hypothesized that this is due in some cases to the low spectral resolution or in part to the relatively low participation of scientists as physicists or chemists in such works that have the necessary skills required to rationalize the spectral data. In some cases, the use of spectral information was slightly improved and has been used to pigment identification and for selection of the colorant materials for retouching some areas (inpaintings) from spectral estimation [56] or to recognize and monitor some materials of historical documents as inks or dyes [33].

Generally speaking, it can be considered that some research works focus more on the spectral information than the previous references discussed. Such kind of approach is more interesting for the purposes of this doctoral dissertation and some examples will be taken into account.

Mansfield et al. have used a combination of a CCD camera and a liquid crystal tunable filter (LCTF) with an illumination system composed by a pair of quartz halogen floodlights to collect spectroscopic images in the NIR range from 650 to 1050nm with a spectral resolution of 10nm to study a drawing significantly altered during a cleaning operation [5], an ink and pen drawing (probably a preparatory design for the elaboration of a stained-glass window) of the 15th century and an oil and tempera painting of the same period [29, 35]. The instrumentation was developed at the institute of Biodiagnostics of Winnipeg (Canada) for the non-invasive investigations of tissue health and despite its limited wavelength range and relatively coarse spectral resolution it was able to recognize some materials as charcoal and to expose under-drawing features.

The research group formed by A. Casini, M. Bacci, M. Picollo and collaborators of the Institute of Applied Physics "Nello Carrara" of the CNR-IFAC at Florence has thoroughly investigated the potentialities of fiber-optic reflectance spectroscopy (FORS) to characterize constituent materials and degradation products of paintings. They have demonstrated that reflectance spectroscopy in visible and in the short-wavelength are powerful non-invasive tools as it can be seen in different works [14, 17, 57]. This research institute has collected a lot of data and some of them are available online on the database "Fiber Optics Reflectance Spectra (FORS) of Pictorial Materials in the 270-1700 nm range" [58]. They have also evaluated the potentialities of Imaging Spectroscopy concluding that the reflectance spectra obtained with both techniques are in good agreement [1]. On the late nineties, they used an imaging setup that was constituted by a lead oxide-lead sulphide PbO-PbS vidicon camera and a set of 29 narrow-band filters in the wavelength range from 420 nm to 1550 nm and an illumination system composed by two projectors (150W quartz tungsten-halogen lamps) placed at ~45°. The distribution of the 29 images was every 20nm in the 420-700nm range, every 50nm from 750nm to 1200nm and at 1300nm, 1400nm, 1445nm and 1550nm. The images obtained on a tempera panel painted with four known pigments were studied with Principal components analysis (PCA) in order to perform a methodology able to detect areas with different chemical or physical properties to analyze artworks. In fact, the developed method was applied to the study the painting of Luca Signorelli "Predella della Trinità" mapping regions with similar spectral signatures [59,60]. This imaging spectroscopy device was used to study the important panel "La strage degli undicimila martiri" realized by Pontormo around 1530. The investigation focuses principally on the identification and distribution of certain pigments (goethite and lead-tin yellow) on the surface of the painting [22], comparing IS and traditional wide-band reflectography. IS assisted in the identification of possible overlapping areas of the two pigments. A similar system, covering the range from 400nm to 1700nm with a spectral resolution of 20nm in the VIS and of 50nm in the NIR region, was used to investigate a set of very fragile drawings on paper by Parmigiano [28]. Although the measurement methodology did not provide a clear identification of the constitutive materials, it allows the differentiation between different areas. More recently, they have proposed an hyperspectral scanner based on a prism-grating-prism line spectrograph connected to a CCD camera operating on the range from 400nm to 900nm and a spectral pitch of 0.89 nm (447 images in the sequence) as an innovative methodology for investigations of historic surfaces and wall paintings [14, 34]. The scanner device covered a maximum area of about $1m^2$ and the illumination system consisted of a 3200K 150-Watt QTH-lamp sent to the surface by two fiber-optics with a geometry of 45°/0°/45° fixed to the scan head.

Balas et al. have studied an illuminated manuscript with Laser Induced Breakdown spectroscopy and an hyperspectral imaging apparatus [30] developed and patented by one of the authors, C. Balas [61]. The system acquired narrow band spectral images that cover the spectral range from 400 nm to 1000 nm with an imaging monochromator able of a 2-nm tuning step and coupled with a two-dimensional detector array. It recorded a fully resolved diffuse and/or fluorescence spectrum at each individual pixel representing the sample. They have identified certain pigments and their spatial distribution. Their hyperspectral imager (“MUSIS”) has been implemented and tested augmenting the wavelength range to 360-1150nm (extended to 1550nm when coupled with a photocathode tube) and applied on the study of palimpsests (twice written manuscripts) [21, 62].

Delaney et al. have used visible to shortwave infrared (SWIR, from 1 to 2.5μm) multispectral imaging to identify and map some blue pigments (Prussian Blue, Ultramarine Blue and Cobalt Blue) in two paintings of Vincent Van Gogh, *La Mousmé* and *Self portrait* [63]. In order to differentiate these colourants, they used a CCD camera in the visible (450-700nm) and the NIR (near infrared 700-1000nm) and a PtSi camera on the SWIR (1000-1600nm) as detectors combined with several broadband filters and an illumination system of quartz halogen lamps. Recently, they have reported the identification and mapping of the main colorants used by Pablo Picasso on the painting *Harlequin Musician* using Vis-NIR-SWIR reflection and VNIR luminescence imaging spectroscopy [23]. The instrumentation used for this purpose was composed by two commercial hyperspectral cameras (in the visible and near infrared region, VNIR, and in the SWIR region) and by one homemade multispectral luminescence imaging spectroscopy camera system. The VNIR imaging spectrometer is a slit based, scanning hyperspectral sensor which uses a grating spectrometer as a dispersive element and a Si charge-coupled device (CCD). The system is responsive from 417 nm to 973 nm with a spectral resolution of 2,25nm. The SWIR imaging spectrometer is a slit based, scanning hyperspectral sensor with a grating spectrometer used as a dispersive element and a InGaAs array sensor. This device obtains 85 images separated approximately by 10nm from 895 nm to 1749 nm. The samples are diffusely illuminated by two 1000W halogen lamps at 50 degrees from its normal with UV filters to block the harmful radiation. The multispectral luminescence imaging spectroscopy was realized with a system operating from 650 to 900 nm in six bands which obtains the relative radiance image cubes by means of a CCD camera and a set of spectral interference pass bands filters. In order to induce the blue/green excitation two slide projectors with 380-520 nm filters at about 45 degrees from the normal to the sample were used. The results show the potentialities of imaging spectroscopy, in particular when different devices that work in various modalities and spectral ranges are used. Moreover, when they are complemented by another non invasive technique as XRF, they suggest the possibility to use such approach as a robust tool to identify and map pigments. Lastly, Delaney et al. have used multispectral visible-infrared (400-2500nm) reflectance and luminescence imaging spectroscopy to determine and localize pigments on medieval illuminated manuscripts. They used two camera systems in order to obtain 15 visible to infrared reflectance and 7 luminescence images to identify lapis lazuli as instance [64].

The studies exposed previously are the most interesting imaging spectroscopy methodologies for the purposes of this doctoral dissertation over the last two decades. On Table I.1 on next page, the main characteristics of these systems used on the cultural heritage area are summarized. It can be stated that imaging spectroscopy technique still is in its early stages of development in this field and this fact renders this research work of particular interest.

Table I.1 – Main characteristics of some multispectral and hyperspetral imaging systems used on the field of cultural heritage

REFERENCES	**DETECTORS**	**ILLUMINATION SYSTEM**	**SPECTRAL RANGE (nm)**	**DISPERSING ELEMENT**	**SPECTRAL RESOLUTION/ NUMBER OF FILTERS**	**APPLICATIONS**
[5, 29, 35]	CCD	quartz halogen floodlights	650 - 1050	LCTF	10nm	- ink and pen drawings - paintings
[22, 59,60]	PbO-PbS vidicon	150W quartz tungsten-halogen placed at 45°	420 - 1550	Narrow-band Optical filters	29 (20nm from 420-700nm, 50nm from 750-1200nm and at 1300, 1400, 1445 and 1550nm)	- paintings (including replicas)
[28]	PbO-PbS vidicon	150W quartz W-halogen at 45° with UV-cutting glass	400 - 1700	Narrow-band Optical filters	32 (20nm on the VIS region and 50nm on the NIR region)	- drawings in paper
[14]	CCD	3200K 150W QTH-lamp 2fiber-optics 45°/0°/45°	400 - 900	prism-grating-prism line spectrograph	spectral pitch of 0.89 nm (447 images in the sequence)	- historic surfaces - wall paintings
[30]	CCD	Polychromatic UV-Vis-IR	400 -1000	Imaging monochromator	2nm tuning step	- manuscripts
[21]	CCD	Polychromatic UV-Vis-IR	380 -1000	Imaging monochromator	3nm tuning step	- palimpsests
[62]	CCD	Polychromatic UV-Vis-IR	360 -1150	tunable optical filter	34 spectral bands	- palimpsests
[63]	CCD (VIS-NIR) PtSi (SWIR)	500W, 3200K quartz halogen lamps	450 - 1600	Optical filters	8 VIS-NIR and3 SWIR	- paintings
[23]	CCD (VIS-NIR) InGaAs (SWIR) CCD (luminescence)	1000W halogen lamps at 50° slide projectors with 380-520nm filters at ~ 45° (luminescence)	417 – 973 VIS-NIR 895 - 1749 SWIR 650-900 luminescence	grating spectrometer interference pass bands filters (luminescence)	- 2,25nm VIS-NIR - ~10nm SWIR - 6 spectral bands Luminescence	- paintings
[64]	/	/	400-2500	Optical filters	15 spectral bands VIS-IR reflectance 7 spectral bands Luminescence	- illuminated manuscripts

I.E Opportunities of Imaging Spectroscopy considering other relevant techniques used in the cultural heritage field. Possible role on a multitechnique approach

As it has been said before, Imaging Spectroscopy is a non-invasive technique, which means non-destructive, without sampling and contact. It is also possible to build transportable devices, in order to realize analysis *in situ*. These characteristics are two of the principal advantages of this technique. There are several advanced methods used to study cultural heritage materials that require tiny samples to be employed, in cross sections as instance. However the use of microdestructive techniques has important drawbacks that must be considered. The sampling procedure, even when it is minimal, is not advisable when dealing with irreplaceable or precious objects. Moreover, microsamples are normally obtained from some edge or *lacuna* and they may be not representative of the object under study. This fact justifies the increasing interest in the research and use of non-invasive analytical techniques able to yield information by remote examination of the entire work of art under consideration and the possibility to integrate these methodologies. If the analysis can be conducted in a non-invasive way and *in situ* then the conditions are optimal in order to study cultural heritage objects. The possibility to perform the analysis with portable instrumentation to such unique samples as those regarding the field of cultural heritage have several advantages as avoiding any transportation risk and cost. If the study is executed *in situ* it is possible to investigate a large number of works of art, in a museum as instance, and to discuss the preliminary results and other important factors with the conservators, restorers and curators [65]. In some cases, as when dealing with mural paintings, it is not even possible to move the artworks and the only choice, if sampling is not possible, is to recur to transportable devices.

The non-invasive and *in situ* approach has, as a consequence, the fact that no sample preparation is needed. From a certain point of view, this is an advantage because many operations of this process are delicate and time consuming. However, this also supposes that samples are normally complex, heterogeneous and often layered systems and the information collected is difficult to be elucidated. Moreover, transportable devices are built achieving a compromise between efficiency and portability and in many cases the analytical power of instruments are not the same as in laboratory conditions. Furthermore, one of the strong limitations of this kind of approach is the characterization of different layers typical of the samples of cultural heritage area. For example, to resolve the complex stratigraphy of a painting is a really delicate operation and normally microsamples are required in order to be studied by different techniques as optical microscopy (OM) or scanning electron microscopy-energy dispersive spectrometry (SEM-EDS). Nevertheless, the possibilities of the non-invasive and *in situ* approach are demonstrated by the fact that there are different research groups, some of them afferent to conservation institutes as the Getty Conservation Institute or the Centre de Recherche et de Restauration de Musées de France, that have adopted such methodologies [65]. This kind of approach have limitations as the impossibility to totally resolve the stratigraphy of a painting a lot of work has been done and much more must be done in this field in order to obtain as much information as possible using such methodologies. Due to the characteristics presented by Imaging Spectroscopy, it can be an integrated part of a multitechnique non-invasive *in situ* approach.

IS instrumentation can be relatively inexpensive. As it has been considered in the precedent section regarding the state of the art of imaging spectroscopy, a significant part of the IS devices used in the cultural heritage field are home-assembled, as the one used in this doctoral dissertation (that will be commented and discussed on a subsequent chapter). In some cases, as in this research project, the aim is to design and to build a robust and cost-effective system. This aspect is another considerable advantage of the imaging spectroscopy technique because, for financial reasons, it is necessary to find a balance between the instrumentation performances (in terms of wavelength range or spectral resolution as instance) and the need for reasonable costs.

Some of the *in situ* techniques in widespread use, such as XRF, FORS or Raman Spectroscopy, are point measurement techniques, thus they are performed on very small paint areas and applied to a limited number of sites of the cultural heritage objects. Since the samples of this field are normally highly heterogeneous, the results obtained on these selected spot may not be representative of the neighbouring regions. Several of the non-invasive and portable techniques, such as FORS or XRF, could be used to scan the entire surface of the sample, but the long times required make these procedures adequate only for small sections [23]. FORS scanning technique can be replaced by an imaging device: a non-invasive method which records reflectance and emission spectra of the entire samples surface, therefore by achieving imaging spectroscopy. This is a great asset of this technique because it allows not only the characterisation of some materials but also its spatial localisation and distribution, thus performing mapping. To record the acquisition scene is really important in cultural heritage field, not only because of the highly heterogeneity, but also in order to achieve monitoring, because with spot techniques repositioning at the same points where the analysis was performed in a previous measurement campaign is more difficult than using a mapping technique to reach this purpose. In addition to that, maintaining the visual aspect of the collected data allows having a handy interface that can be used also by the restorers or curators of the samples. Moreover, imaging spectroscopy can be used to locate areas where further analysis are required, so where punctual techniques can be accomplished or where micro-sampling could be necessary, in order to reduce this destructive operation.

Imaging spectroscopy is able to collect huge amount of data in relatively short times: it gathers the reflectance spectra per single pixel of the digital reconstruction of an image which represents the sample surface. In the visible, this data allows the definition of the colour through the colorimetric coordinates. This information permits to obtain digital version of traditional photographic reproductions, to monitor changes and damages, to assist in the restoration processes assessing damages from cleaning procedures or through virtual restoration and to characterize, to differentiate, to map and to monitor materials of cultural heritage samples revealing original and retouched materials. This huge amount of data creates new opportunities but also poses data mining challenges. Indeed, it is difficult to rationalise, manage and handle the collected information and to process it, a software program, specially developed or commercially available, is needed. Hyperspectral images are usually very large files, usually up to several hundred megabytes so data storage also must be considered.

Other disadvantages of the imaging spectroscopy technique are the rationalization of the obtained spectra since cultural heritage samples are complex mixtures and its fingerprinting ability in comparisons with other techniques as Raman spectroscopy is inferior.

Finally, there are other drawbacks that depend greatly on the characteristics of the instrumentation. As instance, systems based on sensor array suffer from pixel-to-pixel biases, lens distortion and non uniform illumination. All these factors must be considered and studied in order to plan correction procedures [51].

A fundamental factor to take into account when dealing with IS technique concerns the performances of the detector, and more precisely, the wavelength region covered by the device and its spectral resolution. This technical specification is closely related to the conservation problems that can be solved. The frequencies used to irradiate the samples are of great importance: it must be kept in mind that the penetration depth of the radiation and the information obtained from the sample depend of this characteristic of the incident beam of light. This must be considered in order to understanding the provenance in terms of depth of the data collected but also when the information gathered with different techniques is integrated. For example, if data acquired by XRF and FORS are compared, it must be taken into account that X-rays are more penetrating than UV-Vis-NIR light and the depth volume considered with both techniques is different. Imaging spectroscopy is normally performed in the UV-VIS-IR range. Considering this region of the electromagnetic spectrum it can be said that since most pigments are transparent to NIR wavelengths, Imaging spectroscopy in this region of the electromagnetic spectrum can be used to study for example features that underlie the paint layer, such as under-drawings and *pentimenti* [51]. In fact, IR reflectography which is performed by acquiring an IR image in a single large band, is widely used to study such characteristics. On the other hand, UV radiation is less penetrating than the latter and it can be useful to study some substances that exhibit a characteristic fluorescence emission under UV illumination. This property can be applied to differentiate some materials such as resins, varnishes, pigments or conservation materials as the consolidating resin paraloid B72, but a lot of care must be taken because UV radiation can be harmful to delicate materials such as paper-based artworks [25, 28]. In the present doctoral dissertation, the wavelength range used is mainly the visible and the main applications are the characterisation of pigments and colorimetric measurements. The study of the colouring agents used to complete an artwork is fundamental to have a thorough understanding of the history and of the technique of execution of an object. It is important for dating and attribution purposes and also for the detection of materials applied later, for restoration purposes as instance, in order to select restoration products that prevent incompatibilities, to provide criteria for an adequate conservation project or to monitor after an intervention process.

There are few works where it can be seen that Imaging Spectroscopy represents a powerful tool that completes the information acquired by other techniques used in this field as LIBS [30] or XRF [23]. Despite its potentialities, it is not still a well-established component of the most important mobile laboratories of this research area as the MOLAB, which exploits an integrated suite of non-invasive spectroscopic techniques [65]. Taking in consideration the huge amount of information that can be collected with IS technique and its performing characteristics, it can represent a valuable component of such type of multitechnique approach, as the results of this doctoral dissertation will show.

When a work of art is under study, the scientists must select the most adequate techniques on the basis of the problem that must be solved. The choice of the technique is determined by the equipment availability and the information provided. The data obtained with one method must be completed with the ones collected by another measurement system, in order to acquire as much information as possible and elaborate a robust conclusion from experimental evidences. Three techniques are widely in use for the characterisation of pigments *in situ* and in a non-invasive way in artworks are XRF, Raman and FORS spectroscopies.

Raman spectroscopy and especially Raman microscopy have many applications in scientific studies in the field of cultural heritage, it has been claimed that is the ideal analytical method for pigment analysis due to its reliability, sensitivity and possible adaptation to *in situ* application [1, 15, 66]. However, despite its many advantages, there are two important drawbacks that may hamper a Raman measurement. One of these disadvantages is the presence of fluorescence that overwhelms the Raman spectrum because it is much more intense than the Raman effect. Other drawbacks are its need for stability, and the difficulty, in some occasions, to record spectra of sufficient quality and its interpretation, especially when dealing with mixtures.

FORS spectroscopy is an appealing technique that has many uses in the field that studies cultural heritage objects as the characterisation of pigments. Instrumentation can be relatively inexpensive, measurement are non invasive and equipment is portable [14, 18]. However, reflectance spectroscopy has poor fingerprint ability in comparison with other techniques such as FTIR [25].

XRF analysis allows the determination of most element of the periodic table, in major, minor and trace concentration. The operation costs are low and the analysis time is short. The identification of materials is attained through the presence of key-elements. However its limitation to detect light element due to the absorption by the detector and the atmosphere is an important drawback, in particular when dealing with organic materials, for example in the identification of dyes and lakes [13, 15].

Observing the characteristics of these techniques, it is evident that a multitechnique approach is really convenient because the techniques can be integrated to collect as much information as possible, and the drawbacks of a technique can be covered by the analytical power of another. There are several examples where these techniques have been integrated in order to identify different materials as pigments [13, 15, 65].

Taking into account the kind of information obtained by Imaging Spectroscopy technique, it can represent an integrated part of such multitechnique approach. Information acquired from reflectance spectra has proved its analytical power to study artworks when it is complemented by Raman spectroscopy data [12]. From a certain point of view, IS extends the capability of conventional imaging and spectroscopy, improving FORS technique. However, both techniques can even be integrated, IS can individuate areas of interest where it is interesting to study reflectance spectra in a more accurate way. The elemental information provided by XRF can be complemented by IS data, achieving robust pigment identification and mapping as some authors have suggested [23]. In this doctoral dissertation, the multitechnique approach that has been adopted integrates IS and XRF technique. This choice is justified by the fact that both techniques are non-invasive, portable, relatively fast and handy, adaptable to different measurement conditions (this feature is extremely important taking into account the difficult measurement conditions that can be faced when studying cultural heritage objects as the lack of space) but above all because of the possibility to complement the information obtained with both of them. The key-elements provided by XRF and the analysis of the reflectance spectra collected by IS give information useful to characterise the colouring agents of artworks and their spatial distribution. The usefulness of such approach will be discussed on a further section where some results obtained on a mural painting and on stained-glass windows will be presented and discussed.

Chapter II : Paintings and Glass objects

In order to understand the variegate issues related to cultural heritage objects it is necessary to have a detailed knowledge of the type of materials used in this particular field. Artists and craftsmen have used every kind of materials at their disposition since the beginning of civilisation. It is possible to find objects made of metals, glass, wood, minerals, gemstones, tissues, plastics, etc… It has always been a human prerogative to experiment with different and new materials in order to create objects that could be artworks or articles for diverse uses. To comprehend the ageing processes suffered by a work of art, to individuate the conservation conditions or to define the best restoration products in order to prevent further incompatibilities it is necessary to have a deep knowledge of the materials in terms of composition but also of stability to light, temperature, pollutants agents…. Moreover, in order to elaborate a thorough and realistic analysis, when a cultural heritage object is studied this acquaintance is required otherwise the collected data can be misunderstood.

In this chapter a brief description of the structure and composition of some objects and materials used in the cultural heritage field and of interest for this doctoral dissertation will be given. In future sections, the study of pigments on a mural painting and of the chromophores of the glass *tesserae* used in stained-glass windows will be faced. For this reason, in this chapter the basic organization and components of this kind of objects will be presented, paying particular attention to the colouring agents. First of all, the structure of a painting and the composition of the main components will be provided. Some characteristics of pigments and dyes will be discussed, included some regarding their stability. Lastly, some basic topics regarding mosaics, stained glass windows and the vitreous state will be considered. This chapter will allow to face the following sections with a better understanding of the issues that must be contemplated.

II.A Paintings

II.A.1 BASIC STRUTURE OF A PAINTING

Paintings are essentially two-dimensional images painted on a flat surface. Whatever the final result is, it is composed by the same basic components as a superimposition of layers. The surface upon which the paint is applied is known as the support which can be a flexible material like cotton or linen canvas or rigid like panels of wood, metal, glass, plastic or walls and ceilings. The second layer is called preparation layer, usually made of size. Size is a diluted glue, most typically made from animal skins. The size prevents the binder in the subsequent layers of the painting from being absorbed into the support, thereby weakening the painting. In addition, it prevents the penetration into the support of binders and vehicles that may have a deleterious effect on the support material. This preparation layer may also include a ground that covers the sized support to further protect it from the adverse effects of the components of the other layers, to block the absorption of the binder into the support and to homogenize the surface allowing the overlying layers to adhere uniformly. The ground is essentially a paint, made of materials compatible with the support material and the paint layers to be used over it. A generally white mixture (sometimes called *gesso*) of animal glue and normally a white pigment as chalk (calcium carbonate) has been used for centuries as a ground for both wooden panels and canvas. The most common ground preparation used today is one containing a binder of acrylic polymer, which replaces the animal skin glue used in the traditional one. Traditional grounds produce an opaque surface that, in addition to its protective function, also acts as a reflective surface beneath the paint film. When light interacts with the painting it may penetrate as far as the ground. If it is reflected back by a dense white surface, it will be perceived as luminosity in the painting, a quality required by many artists. However, some grounds are not white. The painter may decide to add certain colours to the ground mixture to act as a base for overlaying colours. A cool tone (blue-gray or green) sometimes underlies the warm colours of flesh. A thin layer of colour called *imprimatura* may be applied over the ground to act in a way similar to a toned ground, and may also serve to seal the preparative layer. Painters sometimes find these colours useful as the painting develops. Areas of either toned ground or *imprimatura* may be visible in a finished painting. For example, Tintoretto (1518-1594) used to paint on a black background and Veronese (1528- 1588) used to paint on a green background [11, 67].

The following layer is made by the sketch that is a preparatory drawing of the picture made with charcoal or metal points, for instance. At this point, it can be found the more evident layer to the naked eye: the paint layer. This stratum is composed by pigments, the colouring agents which are most typically fine powders of organic or inorganic material. Pigments are dispersed in a medium, which allows them to be spread out and which binds the individual powder grains together and to the surface to which the paint is applied. This medium, called binder, can be composed of different materials as oils, egg, gums, or synthetic polymers (acrylic, alkyd). It has the characteristic that when it dries it produces a stable paint film. A third component that is not always present is the vehicle, or thinner. The vehicle is compatible with the binder, for example water with egg, gums, and acrylic polymers; turpentine or petroleum distillate with oils. When mixed with the pigment and binder, the vehicle allows the paint to be spread more easily and makes it a bit more transparent. It may also assist in the drying of the film. In all cases, the vehicle evaporates as the paint layer dries [67].

The painting may be coated after its finalisation with a thin layer (or layers) of varnish. It is a transparent liquid material that performs two primary functions: it protects the paint film from abrasions, pollutants in the atmosphere, moisture, dirt… and it can alter the reflective characteristics of the paint enhancing the colours of the pigments. The painter may find that certain colours have dried matte while others have dried glossy. Depending on the desired effect it can be applied as instance a layer that will make all colours uniformly brilliant. Varnishes are made of resinous materials and can be combined with siccative oils or volatile solvents. The resins are extracted from plants for example sandarac is obtained from Cupressaceae or mastic from Anacardiaceae. They can be also produced from fossils as ambra from *pinus fossile* or exuded by insects as shellac *Laccifer Lacca*. Their composition is complex and depends on the botanic and geographic origin, but can mainly be reconnected to the terpenoid class (multiples of the isoprene C5 unit) so they are water-insoluble products. The opportunity to use polymeric materials has been experimented too [11, 67].

Figure II.1 shows a representation of the basic structure of a painting that has been just described.

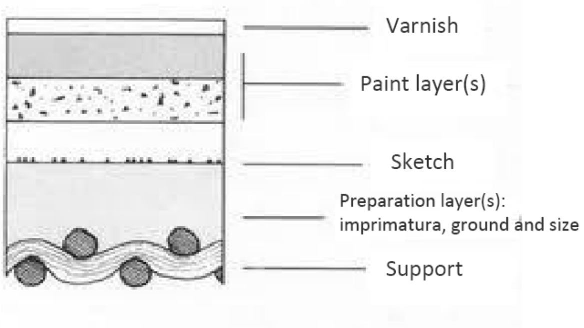


Figure II.2- Scheme of the basic structure of a painting

This structure can be the basic stratigraphy when a cross-section of a painting is observed under the OM as instance and it has been followed by many authors of paintings in the history of the Western art but obviously there exist many variations of this subject. Nevertheless, this scheme represents generally the organization of such kind of cultural heritage objects and it is important to keep it in mind.

As it has been said previously, imaging spectroscopy on the visible range can be used to characterize the pigments of the paint layer, so, for this reason, in the next section of this chapter the composition of this layer will be deepened. Due to the application of the IS technique during this research work to the study of a mural painting that has included the realization of *replicas,* this particular type of artwork will be commented more intensely on a further part of this section.

II.A.2 THE PAINT LAYER

As it has been said before, the paint layer is basically composed by a mixture of pigment particles and a binding medium, the grains provide the colour and the binder joins together the particles that gives the hue and adheres to the support. A paint layer may also contain a vehicle that dilutes the pigment/binder dispersion, allowing the mix to be spread more easily. Other materials may be added to the mixture to enhance the optical or textural characteristics, or to alter the working properties, by accelerating or slowing the drying of the film or by making it more or less fluid. The choice of materials for these various functions is dependent upon the type of support that the painter intends to use, the dimensions of the artwork and the tactile and optical characteristics suitable to the intentions of the executor. The pigment must be dispersed, or ground*,* as evenly as possible in the binding medium to take full advantage of the properties of both elements. Traditionally, the pigment and binder are first mixed into a stiff paste. This is then ground on a flat plate of glass or stone with a flat-bottomed glass or stone instrument held in the hands and pushed in a circular motion. Although some painters today still grind their paint by hand, most purchase their paint pre-ground by machines used by manufacturers to produce large quantities of paint of uniform consistency and pigment distribution. In Figure II.2 on next page, it is shown a schematic representation of the paint layer.

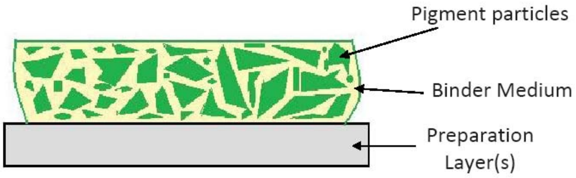


Figure II.2- Schematic representation of a paint layer

Since the beginning of the elaboration of painting, a variety of binding media to spread the colour has been used, ranging from natural gums and oils to proteinaceous materials such as egg (glair and tempera), milk (casein) and collagen glues made from animal skins and skeletons, as instance. Specific knowledge of the nature of the media used in a particular artwork may offer some indications of its state of conservation. Oils and fats are the glycerol esters of aliphatic acids, the most common encountered are the saturated acids with 12, 14, 16 or 18 carbon atoms, known as lauric, myristic, palmitic and stearic acids respectively. The drying power of such acids is related to the presence of sufficient di- and triunsaturations that allows them to react between them and with the oxygen present in the atmosphere to form a polymeric network, giving rise to a semi-solid. Drying oils have been employed broadly as binders because of their skill to form paint films with good optical and mechanical properties in a convenient time. The most commonly utilized in western Europe are linseed, walnut and poppy oils, and in most recent years safflower and tung oils have become more frequent. Wax has been used as a binding agent in paint since antiquity using the encaustic technique which consist in melt this organic material by heating together with pigments and apply the liquid mixture on the dye surface. In some cases, the wax is solved with drying oils or egg yolk. The most widely used as a painting material has been beeswax. Chemically, they are composed by hydrocarbons, tri-, di- or mono-esters of medium length fatty acids, long chain alcohols, free long alcohols, aldehydes, ketones, β-diketones, sterols, triterpenols and triterpenic acids. Their chemical compositions depend on their provenance from animal, vegetal or mineral. Animal and fish collagen glues are proteinaceous materials present in skin and bone that have been widely used as adhesives for wood and as binders in the preparation and elaboration of size of canvas, of the ground and of the paint layer and for. Casein is a mixture of phosphoproteins found in milk products that has been employed as binder, varnish and sealant over primers, grounds and adhesive. Tempera refers to paint containing as binding medium egg, both albumen and yolk. Its vehicle is water, which dilutes the paint but evaporates during the drying process. There are various recipes for the elaboration of egg-based binding media including the presence of other components as linseed oil (*tempera grassa*) as instance. This binder produces a very durable but somewhat brittle paint film. Gums are polysaccharide materials exuded from plants as instance, they can be either water-soluble or water-dispersible. Plant gums has been frequently applied as adhesives and binders from centuries, as the arabic or the cherry gum. Nowadays, synthetic resins such as acrylic, alkyd, polyvinylacetate, or cellulose nitrate, serve as binding media in the vast majority of pictorial artworks. Acrylic paint is based on an emulsion suspended in water. This resin is based on natural materials and has many uses in industry. To make a binding agent for paints, it has to be made into a fluid solution by the polymerisation of acrylic and methacrylic acid, to obtain a white solution which dries perfectly clear. The first acrylic products were developed in Germany during the 1920s and 1930s. From the beginning of its use, artists have been attracted by its ability to dry quickly and by the tough, flexible film it produces. The selection of the binding media was determined by the historical period, the geographical location and the desired effect by the painter [67-71].

The binding media is essential in order to understand many issues regarding the chemistry of cultural heritage field. On this research work, imaging spectroscopy is used to obtain the reflectance spectra in the visible range of different regions of interest. Through these data it is possible to characterize pigments, unfortunately to identify the binding media used, other techniques are required. As it has been said before, the presence of varnishes and binders among other components affects the optical properties and can produce yellowing of a painting, so their presence must be relatively considered when dealing with Visible diffuse spectra. Nevertheless, the fundamental components of interest of the paint layers in this doctoral dissertation are the colourants.

II.A.3 COLOURANTS

The general term colourant includes organic and inorganic materials that give colour to a substance, including natural plant dyes, synthetic pigments or fluorescent brighteners. In the process of the production of paint films, it is necessary, as a starting point, to distinguish between dyes (or dyestuffs) and pigments. The term pigment has been defined by the *Color Pigments*

Manufacturers Association (CPMA) especially to clarify the discrimination between a dye and a pigment "Pigments are coloured, black, white or fluorescent particulate organic and inorganic solids which usually are *insoluble* in, and essentially physically and chemically *unaffected* by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light. Pigments are usually *dispersed* in vehicles or substrates for application, as for instance in inks, paints, plastics or other polymeric materials. Pigments *retain* a crystal or particulate structure throughout the coloration process. As a result of the physical and chemical characteristics of pigments, pigments and dyes differ in their application; when a dye is applied, it penetrates the substrate in a *soluble* form after which it may or may not become insoluble. When a pigment is used to colour or opacify a substrate, the finely divided insoluble solid remains throughout the coloration process." [72]. Considering a paint layer, it can be said that pigments are fine powders insoluble in the binding medium and that are applied to the surface as a dispersed mixture. For use as a pigment, the dyes have to be bounded to an inert and insoluble substrate such as aluminium hydrate or calcium sulphate, forming lakes, as the alizarin lake [38, 10].

Pigments are widely employed in different materials and applications. It is a very important industrial area because colour is a vital physical property of virtually almost all objects. The coloured substances have many provenances. Currently the painter has a really varied palette. On the other hand, the options available to artists of the fourteenth through seventeenth centuries, for example, were very limited. The earliest pigments were various coloured clays and charcoal from burned wood [38, 67]. Natural iron oxides give a range of colours and are found in many cave paintings, as it is shown in Figure II.3.

Figure II.3- Some of the range of natural iron oxide pigments

Before the Industrial Revolution, most of the pigments in use were earth and mineral pigments or were extracted from biological sources as madder and alizarin that are extracted from plants and precipitated to form the lake pigments. Some colours were expensive as blue or purple that were associated with royalty because of their low availability. In Figure II.4, some of the minerals that were used as pigments are displayed, on the left side the blue copper mineral azurite and on the right side the red mercury (II) sulphide mineral cinnabar.

Figure II.4- Left: blue copper mineral azurite. Right: red mercury(II) sulphide mineral cinnabar

Since antique times, synthetic pigments have been manufactured as lead white, lead carbonate hydroxide that has been made using close variants of the process known as the “Stack” or “Dutch” process where lead is exposed to the vapours of acetic acid in the presence of moisture and carbon dioxide; the latter is generally provided by fermenting matter (e.g. horse manure), which also provides a constant raised temperature for the reaction. Obviously, control was difficult; obtaining undesirable products as the ‘neutral’ lead carbonate that decomposes into the lead(II) oxide litharge. Another example of a synthetic pigment that has a long story of use is the verdigris, which includes the corrosion products formed from copper and copper alloys during exposure to the atmosphere and more particularly to organic acids, particularly acetic and formic acid. Verdigris, as a pigment, was generally deliberately manufactured for that purpose by exposing copper plates, strips or foil to organic substances such as vinegar or urine. The green to blue encrustation produced could then have been further refined by dissolution in vinegar and subsequent recrystallisation through evaporation [38, 67, 73-75]. In figure II.5, on the next page, the production of the synthetic pigment verdigris is shown.

Figure II.5- Synthetic production of the blue-green pigment verdigris

Prussian blue was synthesized by accident in 1704 and this is considered as the beginning of the era of modern pigments. By the early 19th century, synthetic and metallic blue pigments have been added to the range of blues, including French ultramarine, a synthetic form of the semi-precious stone lapis lazuli, and the various forms of Cobalt and Cerulean blue. In the early 20th century, organic chemistry added phthalocyanine blue, a synthetic organometallic pigment with overwhelming tinting power. In 1856, Perkin, while looking for quinine, discovered the mauveine dye, which is considered the first synthetic route to organic colourants [11, 17, 73-75].

Nowadays, there are really varied types of pigments with particles ground and separated to be of optimum size, features that differentiate them from the ones employed in old paintings. The refractive index of a pigment is essential. For the best opacity or hiding power it is desirable to have scattering and reflection at the pigment surface which is the results when there is a large difference between the refractive index of the pigment and of the paint medium. For this reason, pigments with high refractive index are considered the best ones but when they are coloured they must be used in larger size to avoid too much scattering, because too fine grinding in these cases can generate a loss of colour. The ideal pigment for use in cultural heritage objects would not lose its properties when exposed to sunlight or to atmospheric conditions, would have regular particular size, would be free from impurities or additives that can deteriorate its performances and must be no toxic [38, 67, 68].

In Table II.1, on the next page, there is a brief list of some of the really numerous pigments used in the past and currently to create artworks.

Table II.1 – Some pigments used in the past and in current days to create artworks and some of its characteristic [38, 73-76].

Colour	Pigment	Chemical Composition	Origin	Use
White	Calcium carbonate whites	$CaCO_3$	Various mineral forms, as calcite, rocks as marble, synthetic and biogenic as the coral.	Since antiquity times, widespread use
	Titanium dioxide whites	TiO_2	Synthetic product	product of 20th century technology
Red	alizarin	1,2-dihydroxyanthraquinone	Dye extracts from roots to prepare lake pigment	Since antiquity times
	cinnabar	HgS	Mineral	Since antiquity times. Used until 19th century
	Cadmium red	$CdSe_{1-x}S_x$ and CdS.xHgS	Synthetic product	Commercially available since the 20th century
Yellow/ Orange/ Brown	Cadmium yellow	CdS	Synthetic product	Product since the 19th century
	Orpiment	As_2S_3	Mineral and artificial forms used	Mineral since antiquity, manufactured certainly since early renaissance. Used until 19th century
	Chrome Orange	$PbO \cdot PbCrO_4$	Synthetic product	Synthesized since the 19th century
Green	Malachite	$Cu_2CO_{3(}OH)_2$	Mineral	Since antiquity times
	Chromium Oxide	Cr_2O_3	Synthetic product	Synthesized since the 19th century
	Phthalocyanine green	Cu(II) complex with Cl and Br substituted phtalocyanine	Synthetic product	Accidentally discovered during the 20th century
Blue	Prussian Blue	$Fe_4[Fe(CN)_6] \cdot nH_2O$	Synthetic product	Accidentally synthesized in 1704
	Indigo	Indigotin $C_{16}H_{10}N_2O_2$	Extracted from the leaves of various *Indigofera* species members of the Leguminosae family.	Since antiquity times
	Ultramarine (Lapis Lazuli)	(Na,Ca)8[(Al,Si)12O24](S,SO4)	Semi-precious stone lapis lazuli or synthetic	Since antiquity times from the semi-precoius stone. Synthesized by Guimet in 1828.
Violet	Cobalt Violets	$(Co_3(PO_4)_2)$ and $(Mg_2Co(AsO_4)_2)$	Synthetic products	Co phosphate discovered in 1859. Co arsenate since the 20th century
Black	Magnetite	Fe_3O_4	Mineral	Since antiquity times
	Carbon Black	carbon	Crystalline carbons, Chars, Cokes or flame carbons. Mineral, soots and smokes, Animal and Vegetable materials	Since antiquity times

The pigments of Table II.1 are only few examples of the numerous pigments relative to the cultural heritage field, but they evidence the variety and complexity that can be encountered when dealing with colourants. It is beyond the purposes of this doctoral dissertation to give a thoroughly list of artist pigments. Instead, the specific pigments of interest for this research work will be commented when they would be used or characterized.

II.A.4 CAUSES OF COLOUR IN COLOURANTS

The colour, which is perceived from a pigment as instance, is originated from a variety of physical and chemical mechanisms. The term chromophore refers to a characteristic atom, group or arrangement of atoms which are responsible of the colour of a compound. In the spectral range of UV-VIS-NIR, several spectral transitions between different electronic levels can be observed. These transitions are, in some cases, the cause of the colour in pigments and are the features that can be observed through the IS technique.

Many inorganic pigments derive their colour from the ligand field transitions, such as Chromium Oxide, Malachite or Cobalt Violet. The transitions occur between levels that are localized mainly on a metal ion, that can be a main constituent of the material as in chromium oxide or an impurity as Cr(III) in ruby. The metal ion is surrounded by ligands that produce a field acting upon the metal orbitals, breaking the degeneracy of the d orbitals of the transition-metal. The energy of the degenerated d levels is a function of the geometrical arrangement of the ligands, of their nature and number. The selection rules permit the differentiation between the “allowed” and the “forbidden” transitions. The Laporte selection rule states that the transitions Laporte-allowed involve a variation on the secondary quantum number $\Delta l = \pm 1$. The transitions between d-d levels are Laporte-forbidden and for this reason they are much less intense than the Charge-Transfer transitions. When transition-metal is surrounded by ligands it is possible that some mixing between d and p orbitals or some vibrations of the metal-ligand bond break the symmetry, allowing the observation of such weak bands. On the other hand, the spin selection rule states that during a transition an electron does not change its spin, that is $\Delta S = 0$. The spin-forbidden transitions are extremely weak [1, 38, 77].

The Charge-Transfer transitions are not regulated by such strict transition rules as the ligand field transitions and, as a consequence, they give more intense bands because of the strong light absorption in the UV and VIS range. These transitions are the main responsible of the colour of the ochre pigments and the cause of the black colouration of magnetite Fe_3O_4 or of the yellow one of chrome yellow $PbCrO_4$. These are transitions between localized molecular orbitals of different sites of the molecule or crystal with an electron transfer during the transition. The colour mechanism in Prussian Blue, as instance, is an intervalence charge transfer (or cooperative charge transfer) where the absorption of light produces the motion of an electron from one transition-metal to another having as a result a temporary change in the oxidation state of both metals. The process can take place between two different metals (as in blue sapphire, in which colour is due to the transfer of one electron from an iron ion to a titanium ion during the transition) or "homonuclear" as in Prussian Blue. This pigment is a Fe(III) salt of the hexacyanoferrate(II) anion. There are different varieties of this colouring agent that present different chemical formulas depending on the particular synthesis adopted to obtain the final product. They can be represented as $Fe_4[Fe(CN)_6]_3 \cdot 14\text{-}16H_2O$ or $MFe[Fe(CN)_6] \cdot 14\text{-}16H_2O$ where M is a monovalent ion (M^+: NH_4^+, K^+, Na^+). Observing these chemical formulas, it could be hypothesized that the colour is produced by a ligand field transition but this is not the cause of the strong tinting strength of this pigment. Prussian Blue owes its colouration to the presence in its structure of both Fe(II) and Fe(III) in close positions. The light that is absorbed (Figure II.6) produces a charge transfer of one electron from the low spin Fe(II) to the high spin Fe(III) trough the cyanide which bridges the two ions:

$$Fe^{III}[Fe^{II}(CN)_6]^+ \xrightarrow{h\nu} Fe^{II}[Fe^{III}(CN)_6]^+$$

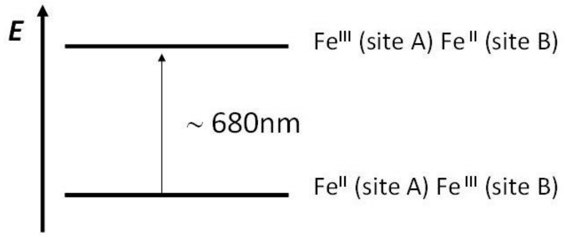


Figure II.6- Charge transfer process of Prussian Blue pigment

This mechanism is also the cause of the deep-blue of gemstone Lapis Lazuli, in particular the entrapped polysulfide radical species S_n^- is the colouring agent and the blue is due to the ligand-ligand charge transfer among the three sulphur atoms of the S_3^- [1, 38, 77].

In many organic pigments and dyes, as for indigo, the mechanism that produces the colour involves $\pi \rightarrow \pi^*$ transitions. They are characterized by very intense bands in the VIS and near UV region. Usually the process involves electrons belonging to several atoms on a “delocalized” system. In a conjugated system the π-bonding electrons are delocalized and the transitions involved occur at lower energies in comparison with a non conjugated organic compound. This transition corresponds to the visible range and not to the UV. In addition, if the conjugated system is accompanied by electron-donor and electron-acceptor groups, there can be a bathochromic shift. This is the cause of the colour of the phtalocyanine pigments as instance [1, 38].

In metals and semiconductors the transitions involved in the production of colour are the energy band transitions. There are many inorganic pigments that are constituted by semiconductors, as cinnabar, orpiment, minium or cadmium yellows, orange and reds. In this kind of compounds, the molecular orbitals, coming from the interaction of the atomic orbitals of each atom, are so adjacent that they produce a continuum. The lower-energy band is filled (the valence band) and the upper band is empty (the conduction band). The energy difference between the two bands is known as band gap or energy gap. In this situation, the interaction with light produces the characteristic S shape in the visible spectrum of these pigments [1, 38].

There are other mechanisms that produce colour but the previous ones that have been described are the principal causes when dealing with colouring agents. It is important to understand them in order to comprehend the data collected when studying an artwork by means of a spectroscopic method as the IS technique.

II.A.5 INCOMPATIBILITIES AND DETERIORATION CONCERNING PAINTINGS

Taking into account the complex structure of a painting and its different and varied components, it seems obvious that, in a heterogeneous system like this, undesirable reactions between constituents can happen. Moreover, a painting is not an isolated system and all of its components can interact with external factors. The feasible interactions may occur between the pigments of the paint layer, or among them and the binding media, the drying agents, the preparation layers, the atmosphere, the light…. Some incompatibilities between pigments have been recognized by artists as a consequence of direct observation of painting deterioration gained through experience. Other adverse results take place in very long times and the undesirable effects are not revealed until they are evident to the naked eye. One of the aims of the varnish layer is to protect the painting from the pollutants of the atmosphere. Nevertheless, it is possible that this stratum is cracked in some areas and in these regions the access to the inner parts of the painting as the pigment particles is allowed by diffusion, permitting a slow attack from atmospheric oxygen, pollutants,.. In addition, some artworks have suffered some extreme conditions produced by fire, changes in aesthetic, abandon… that cause severe damage to these precious objects.

The deterioration, in particular of the paint layer, can have as a consequence the change of its colour properties as the darkening, fading or bleaching of pigments and dyes or the yellowing of the binding media. Fading refers to a loss of colour of the pigments or dyes that can be produced by the splitting of a chromophore group. Chlorine gas, hypochlorite or hydrogen peroxide is used in industry (or at home) to bleach paper pulp or hair. The mechanism involved implies the breaking of a double π-bond that produce a hypsochromic shift to the ultraviolet and the loss of colour. These processes are known as chemical bleaching [38].

Hydrogen sulphide H_2S reacts with a wide range of salts to form sulphides. For example the basic lead carbonate, the most widely used white pigment in Europe since the roman times, reacts with hydrogen sulphide to produce the black galena PbS:

$$Pb_3(CO_3)_2(OH)_2 + 3H_2S \quad \leftrightarrow \quad 3PbS + 2H_2CO_3 + 2H_2O$$

Other lead pigments, as Naples yellow (lead antimony oxide) or red lead (Pb_3O_4), react in a similar way. The chrome and cupper pigments suffer a darkening process in the presence of hydrogen sulphide because they also form black sulphides. There are several sulphur-containing pigments as the cadmium yellow, orange and red, orpiment, realgar or vermillion and the egg yolk contains small amounts of sulphur compounds and they can react directly with lead, chrome or copper pigments to produce the dark sulphides. These interactions may be initiated and/or greatly accelerated by the presence of humidity and UV radiation. These incompatibilities were known, in the *Mappae Clavicula,* a 12th century medieval manuscript where it is specified that orpiment must not be used with lead white and red and 15th century artisans knew that this yellow pigment must not be used with copper containing verdigris. Despite that vermillion is a sulphide, it is less reactive than orpiment and, as instance, it was commonly used in oil-medium with lead white to obtain flesh tints. Hydrogen sulphide damages also fresco paintings on lime-mortar walls according to this reaction:

$$CaCO_3 + H_2S + 2O_2 \leftrightarrow CaSO_4 + H_2O + CO_2$$

$CaSO_4$ has a much larger volume than the former calcium carbonate and this increase in dimensions causes a mechanical disintegration [38, 73-76].

There are some classes of pigments, as the indigo and the alizarin pigments, that fade when they are exposed to ozone from photochemical smog episodes as instance [78]. Oxygen of the atmosphere or peroxides, originated from pollution, can produce oxidation of some components of the paint layers, as the linseed oil of the medium, due to the presence of double bonds or of the copper pigments generating the black oxide CuO. The photo-oxidation of a conjugated system that reacts with the atmospheric oxygen can produce the fading of some pigments. In the presence of moisture the cadmium yellow, orange and red can react with oxygen to produce the white CdO and releasing sulphuric acid:

$$CdS + H_2O + 2O_2 \leftrightarrow CdO + H_2SO_4$$

Acids can deteriorate severely the paintings. They can be produced from the combustion of sulphur-containing fuels (yielding to H_2SO_4) as instance or from the decomposition of some components as varnishes. Carbonate and hydroxide pigments react with acids but in some cases without change of colour. Nevertheless, these reactions can decrease the refractive index and the paint layer, as a consequence, can lose its hiding power revealing underlying features. Other pigments, as the red alizarin lake, are affected by acids changing its colour to orange or the ultramarine that undergoes the “ultramarine sickness” turning to a dull grayish hue that in an extremely acid environment can change completely to white colour [38, 73-76].

As in the case of acids, alkalis are aggressive for some painting materials. This environment is typical as instance of the paintings created using the *fresco* technique (that will be discussed in the next section). Indeed, there are many pigments that can not be employed in this kind of painting execution. Orpiment can not be applied to wet plaster, fact known at least since the first century A.D. as it is written by Pliny and recorded also by Cennino Cennini in the 15th century. Lead white is unsuitable too, because in an alkaline environment and high humidity conditions it is oxidized to the brown PbO_2:

$$Pb_3(CO_3)_2(OH)_2 + 3/2\ O_2 \leftrightarrow 3PbO_2 + 2CO_2 + H_20$$

Copper pigments turn to black CuO when warmed with alkalis. Azurite tends to turn green in the form of malachite or to other green products as the paracatamite $Cu_2Cl(OH)_{3,}$ specially in the fresco environment and for this motivation it has been applied in many occasions to the mural paintings using the *secco* technique. Prussian blue is also not adequate to the lime environment of the *fresco* paintings because it is very sensitive to alkalis turning brown due to the formation of $Fe(OH)_3$ [38, 73-76].

In some cases, the degradation processes involve biological causes (biological attack) because some microorganisms can contribute to the deterioration of some painting components. As instance, the participation of bacteria in the transformation from lead white to lead sulphide has been studied [79] and also it has been demonstrated that lichens and other microorganisms take part in the biodegradation of copper pigments as malachite to moolooite, a copper oxalate [80].

It is possible that there are some undesirable reactions between pigments and the binding media. Lead white is known to react with fatty acids as the stearic acid present in some lipid binding media to form soaps as lead stearate that affect the refractive index. Many metals contained in pigments are known to catalyze the photo-oxidation of linseed oil films as vermilion or copper resinate. The latter pigment is a green glaze obtained from copper salts reacted with resin acids; it disappeared from the palette of the artists because of its tendency to turn brownish due to the photo-oxidation of the resin acids coordinated to the copper [81]. Smalt, in oil-media, is often observed to have partially or totally discoloured. It has been hypothesised that several factors that act individually or in combination can be the reason of such phenomenon: Smalt is a potash glass containing Co(II) and this renders it unstable in alkalis medium, it has a low refractive index and cobalt can migrate from the pigment particles causing the loss of colour [38, 73-76].

Light can produce photochemical reactions that cause as a consequence the fading or other effects on some components of the paint layer as pigments or varnishes. Ultraviolet radiation as instance produces the yellowing of lithopone $ZnS+BaSO_4$ and zinc white ZnS, the darkening of the pigments containing chromates or the photochemical change from the red vermilion to the black metacinnabar [38, 73-76].

Many of the effects that have been discussed are usually catalyzed by the presence of moisture, heat or radiation. Moreover, changes in temperature and in humidity cause differential expansion and contraction between the different layers of the paintings producing cracking that renders these objects more vulnerable to these deterioration processes. Nowadays, advances in this field have created the sub-category of pigments referred to as “high performance” that denotes members of the larger body of pigments, both organic and inorganic, that exhibit enhanced durability, but many artists did not have the possibility to use these materials. An unpolluted atmosphere, controlled conditions of temperature and humidity and the protection against the most harmful part of light are the usual precautions that can be adopted. However, these artworks have been created to be admired and sometimes the conservation conditions are difficult to control. For this reason, it is important to understand these processes, to individuate the best action for maintenance purposes and to monitor the artworks to detect any change and prevent further damages.

II.A.6 MURAL PAINTINGS

Mural paintings are directly executed on a wall, ceiling or other large permanent surfaces. This kind of work of art has been very popular since the very beginning of human civilization. In the story of mural paintings several execution techniques have been used to create this kind of cultural heritage objects but the most popular is the *a fresco* (*fresco, affresco, buon fresco*) due to its characteristics as durability and the rendering of the colours . The basic structure of a *fresco* (literally “fresh”) wall painting is different in its construction from the general discussed in a previous section of this chapter. Basically, it refers to the practice of painting using pigments dispersed into water on to a base of wet lime plaster. The binder is the result of a chemical process, resulting in a mechanical bonding of the particles of pigment. The colour mixture of pigment and water (in some cases the solution where is contained slaked limed is used too) is brushed onto a freshly plastered surface. The plaster is a mixture of slaked lime (calcium oxide, quicklime or burnt lime, in solution with water, forming calcium hydroxide) and an aggregate (sand, marble dust, or a volcanic ash called *pozzolana*). As the plaster dries, the particles of pigment are pulled into the surface, locked in place and protected by particles of calcium hydroxide, which convert to calcium carbonate as the plaster dries, according to the reaction:

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O$$

The plaster acts as ground, support, and binding agent and in this way *Fresco* is the only painting technique in which all of the components merge to form a single unit. Despite its apparent simplicity, this process is complex in its chemical interactions and demanding in its execution. The wall surface is built up of layers of different formulations of lime, water, and aggregate. Each successive layer contains a greater percentage of lime, gradually increasing the binding power of the plaster. Layering ensures even slow drying, which reduces the likelihood of cracking. Because most frescos are large in scale, the *intonaco*, or surface layer, is applied in small sections that can be painted in one day before the plaster dries. These sections are called *giornate*, or a day's work. Each *giornata* must be completed in 4 to 8 hours, after which time the plaster has dried too much to permit the adhesion of the pigment particles within its surface. The painting cannot be revived after the plaster dries to make alterations or corrections without having to chip away the *intonaco* and start over again or using *a secco* technique.

Not all varieties of lime are suitable for use in *fresco* painting. Ideally, the lime is free of Mg and not tinted by Fe oxides. The wall is prepared by combining coarse aggregates into lime putty in the first coat, followed by subsequent coats that may contain a higher proportion of lime and increasingly less-coarse inclusions of aggregates. In the first coats (*trulisatio*, *arenato*) a mix of coarse and medium grind aggregates is advantageous. While this provides a relatively gritty and coarse structure, the in-fill is completed with smaller sized particles. These help to keep the mortar structure slightly damp, when residual water from the *intonaco* layer percolates down into the mortar, thereby giving a longer working period for application of colour to the *intonaco/intonachino* layer. In figure II.7 the mortar layers of the *fresco* technique are represented. It is possible that over the intonaco layer another stratum is applied called *intonachino*, in which the most fine aggregates are used.

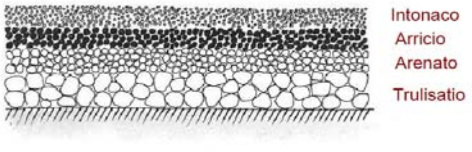


Figure II.7- Mortar layers for a *Fresco* painting

The pigments that can be used on the *a fresco* technique must be chemically inert to alkalis in order to avoid the incompatibilities previously discussed. In order to make retouches or to apply some pigments that are not stable to the alkalis environment, it is possible to perform the *a secco* technique using a binding media when the plaster had set and it is completely dry. The binders that can be used are gums, egg, oils,… There is a third type of technique, called *mezzofresco* or *stanco* which is executed when the *intonaco* is nearly dry, so that the pigment only penetrates slightly into the plaster.

In most cases of *fresco* painting, there is no sense of the surface being coated with a layer of paint. The image is simply a part of the wall, it has the potential to produce brilliant colours as well as a feeling of monumentality through its affinities with architecture. This is due to its particularities that make the pigment particles trapped within the structure of the re-forming calcium carbonate, thereby resulting in a hard-set and durable paint film [67, 68].

II.B Glass Objects

II.B.1 SHORT HISTORY OF GLASS AND SOME VITREOUS OBJECTS

Glass is a material that has played an important role in the history of civilization from its invention up to nowadays, it has multiple uses in the industrial, scientific and technological fields. The discovery of glass is dated back to 7000 b. C.. However, its regular production does not start before 3000 b. C., fact that can be observed from the large number of glass pieces that are present in museums produced in ancient Mesopotamia and Egypt, but also ancient Rome mosaics. Until the first century a. D., the glass was an expensive material, difficult to produce. After this period, the glass became a common material due to the invention of the blow-pipe around the first century a. D., which makes its manufacture less expensive. According to archaeological evidences, it is possible to divide the history of the glass in two main ages. The first one, from the beginning up to approximately the end of the Roman age, is characterised by the glasses called LMG (Low Magnesia Glasses). They are glasses containing low amounts of magnesium and potash (MgO and K_2O below 1.0 % wt). The fluxer used for their preparation is a sodium–based raw material, the *natron,* which is a mixture of Na_2CO_3, $NaHCO_3$ and other species, as of NaCl and Na_2SO_3. The LMGs are typical of the Mediterranean regions as Egypt or Italy. The second age developed after the end of the Roman age and it is called HMG (High Magnesia Glass). The glass shows high amounts of magnesium and potash (MgO and K_2O over 2.0 % wt) that are due to the use of a new fluxer, generally beech wood or plant ashes (*Salicornia Herbacea*, seaweeds in Venice, etc). The HMGs are typical of Mesopotamia, Iran, Central Asia and Northern Europe. The need for a new fluxer was due to economical requirements: after the end of the Roman Empire, in fact, the lack of commercial trades along the Europe forced the glass makers to use raw materials coming from their own territory, instead of buying natron. During the 15th century the production of lead glasses (Bohemia) started and it developed and grew until present days [82-85].

There are many cultural heritage objects that are built with glass or that contain vitreous materials in its structure as jewellery, cups, lamps… For this doctoral dissertation there are two kind of vitreous artefacts of interest, mosaic and stained glass windows. Mosaics are small pieces of roughly coloured squared glass (*tesserae*) in cement on walls or floors to form a picture. They were first developed by the Greeks, and then used extensively in the Roman and Byzantine periods. First, the glass is made opaque by the addition of tin oxide and/or coloured by the addition of metallic oxides as instance. The glass was ladled out in small quantities and pressed into circular cakes. The solidified glass was then annealed, cooled and cracked into *tesserae*. In order to set them on walls or ceilings, a drawing was first pounced, portion by portion, on soft cement that was made of lime mixed with water, pounded brick, gum and white of egg and once made was kept moist with damp cloths while the *tesserae* were set [82].

By far, the most widespread use of glass in the architectural context was in the form of window glass, specially from medieval times onwards. Basically, these objects are composed of glass *tesserae* linked together with lead cames to form a panel (*antello*). In order to secure the panels, they are usually contained in iron frames with crossbars to avoid bulging. Depending on the size of the window, the stained-glass can be composed by few or multiple panels. A number of decorative techniques were used to embellish glass windows, especially those in ecclesiastical buildings. The glass *tesserae* could be bulk coloured or clear glass could be flashed with a thin coating of coloured glass on one side. The panes themselves could be painted, enamelled, stained, etched or engraved. There is an important technique of decoration called grisaille which consists in a vitrifiable paint, mainly made up of transition metal oxides, that was already in use in the XII century. It involves the coloured layers applied on the glass surface in order to draw designs, lines and shadows. It is an essential technique in order to complete the iconographic representation (i.e. faces, clothes, etc.) and the perspective of stained glass windows ('grisaille à contourner') but also to diminish the amount of light passing through a pane (also called ‘grisaille à modeler’) by painting a uniform layer. Taking into account all the elements that compose a stained glass windows it is evident that they are highly heterogeneous and complex systems [82].

In order to optimize restoration and conservation processes and to prevent further degradation of the cultural heritage objects built with glass, it is essential to know as much as possible of their composition, the colourants agents present and the state of their surface. Imaging spectroscopy can deal with the study of the chromophores of such objects. In order to face the experimental part of this dissertation with a better understanding, the next section will deal with some theoretical aspects of the vitreous state, taking particular attention to the colouring agents.

II.B.2 GLASS: SOME GENERALITIES AND COLOURING AGENTS

The ASTM (American Standard for Testing Materials) defines the glass as an “inorganic product of fusion that has cooled to a rigid condition without crystallizing”. However, this definition comprehends materials with a wide variety of compositions. Therefore, commonly speaking, the glass is better described as a “solid, amorphous and inorganic material, produced starting from silica with the addition of alkalis, lime and magnesia” [86]. The basic unit of glass is the tetrahedron of silica, which is represented in Figure II.8.

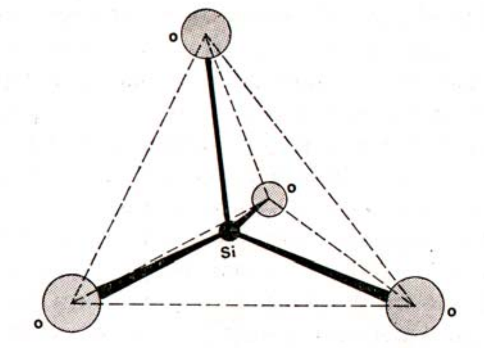


Figure II.8- Basic unit of glass, the tetrahedron silica

It is characterised by the presence of a silicon atom bonded to four oxygen atoms to form a tetrahedron. In crystalline silica, these units are bonded each other in order to form an ordered structure. On the other hand, in the silica glass, the units are disordered and therefore the structure is called amorphous, as it can be seen in Figure II.9.

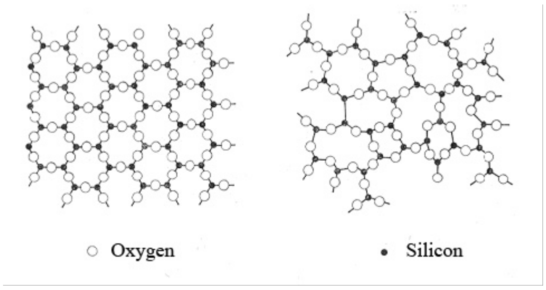


Figure II.9- Comparison between crystalline (left) and amorphous (right) silica structures (the fourth oxygen of silica is below or above the figure plane).

The melting point of pure silica is about 1720°C. This temperature is very high and the common furnaces can not reach it (particularly the furnaces available in the past that used wood as fuel). Therefore, elements as sodium, potash, calcium, and magnesium were added to the silica in order to lower this temperature. These ions are called modifiers, because they stay in the silica network and they decrease the connectivity of the silica structure, lowering the melting point. The oxygen atoms positioned close to the modifier atoms are called "non-bridging oxygen". On the other side, the silicon is considered a network-forming atom, because it contributes to the building of the main glass network. The oxygen atoms that bond two silicon atoms are called "bridging oxygen". In Figure II.10 it is represented the structure of a silica glass with modifier ions in the network. The presence of these elements does not influence only the melting temperature, but also the characteristics of the material as the refractive index or the mechanical resistance [82, 86].

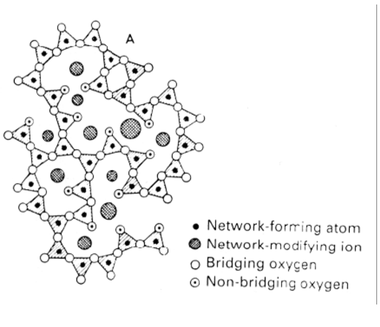


Figure II.10- Structure of a glass containing modifier ions

With the non-invasive technique which is the central object of study of this doctoral dissertation, it would be possible to study the chromophores through the visible spectra, as it will be demonstrated from the analysis of real glassy objects that will be discussed in future chapters. For this reason, the components that are of major interest for this research work are the colouring agents. The final hue of a piece of glass depends not only on the presence of one or more chromophores, its concentration and proportion but also on the vitreous matrix, on the temperature of the furnace, on the environment (oxidizing or reducing atmosphere) during the firing process… The most common chromophores used in ancient glass are transition metals as Fe (III), Mn (III) or Co(II). In this case, the causes of colour are the ligand field transitions. However, it must be kept in mind that this theory cannot be applied rigorously, since a metallic centre may have a wide range of environments producing a broadening of the absorption bands. In other cases, the colour is produced by light scattering due to the presence of colloidal metal particles dispersed in the glass matrix, as ruby glasses in which the red colour is produced by gold nanoparticles. These particles can, in some cases, produce opacity, as in the red opaque glasses of elemental copper or copper (I). Another important group of colouring agents is the semiconductor type as the cadmium sulphide-cadmium selenide system that yield range from yellow-orange to red-black hues. The "beer-bottle" brown arises from a quite complicated mechanism which implicates the presence of iron sulphides: Fe(II) and Fe(III) atoms are surrounded by sulphur and oxygen ions in different geometries and the colour is due to a charge transfer process. Since the raw materials contain iron that could yield undesirable colouration, decolourizers are important components in the production of glass. One of the main elements used to this purpose is manganese. Mn(III) absorbs the light in those regions where Fe(II) does not do so, thus providing a complementary colour and resulting in a uniform absorption across the spectrum. Moreover,in some conditions, Mn(III) can also oxidise Fe(II) giving rise to colourless Fe(III) and Mn(II). Antimony was used too as a decolourizer and as opacifying agent since the ancient time. These agents are important also for the optical properties of glass and must be considered. Tin dioxide was the most used opacifying agent since the V century (A.C.) and lead antimoniate and stannate generate yellow opaque glasses [38, 82, 86-92].

Glass can suffer deterioration processes that are strongly dependent on its chemical composition as well as on the environmental characteristics. These mechanisms are not trivial and will be described briefly. The only chemical reagent that produces an immediate attack to the glasses is the HF. However, glass is not as stable in aqueous solutions as it seems. In fact, vitreous materials suffers in general two degradation processes: leaching (acid attack) and corrosion (basic attack) but they are slow mechanisms which consequences are not evident in early phases. The degradation of glass is based on ion exchange processes on the surface, leading to the formation of salts by reaction with the atmospheric pollutants. Three different layers can be identified in weathered glasses: the unaltered bulk glass, the gel layer composed by a hydrated silica network, and the layer of corrosion salts formed externally. The weathering causes a general modification of the pH at the surface of the glass (e.g. NaOH) and a decrease in the compactness of the structure, with the formation for example of voids in the areas of substitution of sodium by hydrogen. The progress in degradation causes a general decrease in solidity of the glass structure and a loss of cohesion. The general effect is the creation of the porous, fragile and highly hydrated silica gel system, that in many situations proceed with the formation of a white powder at the glass surface, mainly composed of SiO_2. The CO_2 and SO_2, present in the atmosphere as instance, affect glass behaviour during corrosion. In fact, both pollutants generate an increase of the local pH at the surface. For example, atmospheric CO_2 generates carbonates (generally Na_2CO_3 and K_2CO_3 and bicarbonates) which hygroscopic nature favours further glass corrosion. Sulphur dioxide is oxidized in atmosphere and generates sulphates, which quickly exchange with carbonates. The weathering behaviour shows the same mechanism for sodium, potash, calcium and magnesium, but their tendency to degradation is different according to the specific modifier. In fact, the glasses containing potash are more easily weathered than the glasses containing sodium, because potash shows a higher mobility than sodium, due to its lower charge to ionic radius ratio. Moreover, the same considerations could be done about the calcium and the magnesium, but due to their small mobility they poorly acts in glass weathering. The corrosion of the glass can produce opacifying effects that alter the optical properties of the vitreous objects.

Chapter III : The Imaging Spectroscopy system

In the previous chapters, mainly theoretical aspects have been faced in order to have an adequate perspective of the subject. In the present section, some important experimental and technical aspects will be discussed. In particular, the imaging spectroscopy device used in this research work will be described. This system has been conceived and built by the LUXOR laboratory of the CNR in collaboration with DEI department of the University of Padua. The analytical power using an IS device depends greatly on its instrumental characteristics. For this reason, these features will be discussed and some generalities concerning the building of this kind of systems will be commented too. At this point, IS device was applied to study cultural heritage objects of interest, taking particular attention to the chemical information that it was able to collect. Some discouraging results were obtained but these outcomes were useful in order to optimize the acquisition setup. Several of the measurement difficulties that were encountered during the first tests will be discussed. At this point, laboratory samples were specially prepared with two main purposes: 1) individuate the problems presented by the IS arrangement and the parameters that could be improved and 2) understand potentialities and limits of the device. Many aspects have been taken into consideration as the illumination system, the wavelength range, the signal to noise ratio, the spatial and spectral resolution or the calibration procedure. In many occasions, it has been considered useful to compare the spectral information acquired by the IS instrumentation with the one obtained by commercial devices as benchtop spectrophotometers in order to evaluate it with well-established systems. Some of the samples were exposed to accelerated ageing in order to induce changes in their optical properties. Through the measurements with the IS device during this process, the acquisition setup adopted after several improvements was tested and its analytical possibilities were verified. This part, which has the aim to establish an acquisition setup with known analytical skills, had occupied an important and time consuming section of this research work. However, these operations proved to be highly useful when the IS measurement system has been applied to the analytical study of real samples.

As it has been said before, one application of visible spectra can be the characterisation of the colouring agents used to create coloured glass objects. When the artworks are opaque, as in the study of mosaics, the reflectance mode is the unique analytical solution that can be adopted. On the other hand, when the samples are transparent, as many glass *tesserae* of stained glass windows, the examination can be performed both in reflectance and transmittance mode. For this reason, it has been decided to dedicate a part of the research to set up a measurement modality able to acquire visible spectra in transmittance mode using the IS device. For this purpose, homogeneous samples with different optical properties were employed, comparing the results of the developed system with the ones obtained with commercial spectrophotometer. As in the precedent part, the measurements were performed in order to optimize the transmission acquisition setup that afterward has been applied to study the chromophores of real coloured glassy samples and that will be discussed in a further chapter.

This part of the doctoral dissertation is essential because it has established the basis of the rest of the research work.

III.A The Imaging Spectroscopy system

III.A.1 BUILDING AN IMAGING DEVICE

Before starting with the description of the imaging spectroscopy, some generalities of this kind of device must be faced. The principal components of this type of instrumentation are the dispersive element, the detector, the illumination system and the computer. The selection of the single elements depends on the application field, the equipment availability and the financial resources. The illumination system irradiates the sample that interacts with light reflecting or absorbing it. The light can be monochromatic, if optical filters are placed in front of the source, or polychromatic. In the latter case, the dispersive element must be situated in front of the detector that will capture the signal coming from the object under study. Finally, a PC is required in order to store and to elaborate all the information collected.

The dispersive element has the objective to separate the polychromatic radiation into different wavelength components, as a prism that is able to disperse white light into its diverse coloured parts. There are different approaches to reach this purpose. One of those consists in using in front of the detector (or in some cases in front of the illumination system, but this method seems less efficient) appropriate filters. One of the key questions regarding this issue is how many filters are necessary to reconstruct a spectrum of sufficient quality. This depends strongly on the wavelength range and obviously it is conditioned by the function that the device should perform. The interferential filter wheel approach has the advantage of compactness and simplicity but has a low spectral resolution to some requests. Another solution is provided by the use of liquid crystal tuneable filters (LCTF) that have the capability to continuously tune the spectral range with transmittances comparable to those of interferential filters. This technology is promising and covers the VIS and NIR range but, due to the polarization-based filtering process, polarized light might give false reflectance measurement. In systems using filters, a (generally small) number of monochromatic images are gathered, one per filter. In other IS setups, a grating-prism mechanism is used as a dispersive element. Usually, this procedure is adopted in mechanisms that employ 1D line-scanning mechanism in which a 2D sensor looks through this kind of dispersive element (composing the so-called image spectrograph). The 2D array records the spectral information on the axis orthogonal to the entrance slit and the spatial information on the parallel axis: scanning on the first line yield to the reconstruction of a complete spectroscopic image data cube. The commercial product ImSpector [96] is probably the most popular of this family of “image spectrograph” that can be quickly combined with other components to form a spectral camera. Compared to filter-based imaging system, this approach produces full continuous spectral information with high-quality spectral and spatial resolution. However, it has some drawbacks as the pixel to pixel biases, lens distortion or a non-uniform illumination but they can be overcame by correction procedures. Lastly, the computer designed holographic 3D grating gives both spatial and spectral views in the same frame and it could represent an important improvement [4, 8, 25, 34, 51].

A fundamental factor to be considered when building an Imaging Spectroscopy device concerns the performances of the detector, which is crucial and can be regarded as the central component of the system. The choice is closely related to the problem that must be solved, so it depends on the application field. Some important parameters are the possibility to have a real-time spectral imaging (for focusing as instance), high spectral resolution and range, low dark current, high throughput and sensitivity in order to avoid long exposure times of lighting to prevent harmful effects on the samples and capability to interface smoothly with other equipment. However, the first feature to be decided is the wavelength range. In the VIS and NIR range, from 400 to 1100nm as instance, the most popular are the widespread Silicon detectors, as the scientific cooled digital CCD cameras. This kind of sensors is usually blinded to infrared radiation and reaches high spatial resolution through higher pixel density, but in this way photon sensitivity can be sacrificed. To push the wavelength limit of the Si detectors on the UV range as far as 200nm and nMOS (n-type metal oxide semiconductor) technology may be used. On the other hand, to extend the measurement range to farther IR there are different solutions. PbO-PbS vidicon camera extends the upper wavelength limit to 2000nm. PtSi cameras provide excellent images with high spatial resolution but they have the drawback of a dramatic reduction in sensitivity from 1800 to 2000nm. Other semiconductor cameras are available as InGaAs until 2500nm and the HgCdTe up to 3500nm. When the wavelength is longer than 2500nm, the thermal emission of the particles at room temperature is not negligible and the signal can be blended by the temperature distribution. In the UV and IR ranges, the high density multiple pixel detectors are expensive, small and not very common, so in many situations a single detector is used instead of an array and this implies the employment of a XY scanning device that is less suitable for portability purposes. Moreover, the XY translation stages approach has the drawback of being time consuming if compared with systems based on extended sensor. Nevertheless, this kind of instrumentation presents advantages like a wider wavelength range and an image free of aberrations that will save post-processing operations [4, 22, 25, 28, 34, 51].

The illumination system is important, because it must provide the sufficient homogeneous brightness to interact with the sample, in relatively short exposure times and subsequently light must arrive to the detector (imaging devices are open systems and these conditions can imply a loss in the intensity of the radiation) but at the same time it must not be harmful to the objects under consideration that in many cases are delicate and unique. Generally IS requires strong lighting of the surface and this implies problems when dealing with works of art. The ideal conditions mainly combine homogeneous lighting over a large area, no radiation damage to the samples and intense polychromatic emission. The most commonly used illumination system consists of quartz tungsten halogen lights that can be found in slide projector lamps. They emit radiation between 380nm to 1050nm, rated from 100 to 300W in a fairly consistent way leading to stability when the spectra are recorded. The illumination must be as homogeneous as possible and for this purpose the source (or sources) is normally placed at 45° with respect to the normal surface of the sample (also to reduce specular reflection, especially when objects as varnished paintings are analysed). In XY translation stages devices optical fibres can be utilized to obtain even illumination of the small areas considered in this measurement arrangement [4, 25, 34].

In order to complete the imaging system, a computer is required to control all the components, collect and interpret the information. The raw data are initially saved and stored. Then, due to problems as a non-uniform illumination or inhomogeneous responses (of the detector or of the optics as instance) that can occur during the measurement practice, some corrections can be performed, in addition to the ones related to the calibration procedure as the white correction and the dark current subtraction. The information is subsequently arranged as a multispectral/hyperspectral image and to manage this huge amount of data (that can be as large as some gigabytes!) a software is required. There are some specifically developed programs as the ENVI package (Environment for visualizing images: Research Systems, Inc., Boulder, CO, USA). The execution in parallel any operation in any image of the spectroscopic data cube, as calculations or the selection of a Region of interest (ROI), need to be performed by software. For example, the result of this software processing can be the spectra of different areas of the sample. Finally, further elaboration of the data can be performed though principal components analysis as instance, in order to obtain a more meaningful and handy interpretable information [4, 25, 34].

In general it can be said that the final spectral resolution is determined by the number of filters used or in the features of the LCFT or of the image spectrograph. However, it also depends on the storage faculties of the computer and on the capacity of the software to deal with the data because in such cases high spectral resolution produces very large data set that can be difficult to handle. Depending on this factor, the system will be a multispectral or a hyperspectral imaging system. The final spatial resolution is regulated by the number of active elements on the detector, by the optical path, by the sampling grid, by the scanning modality of the area (whether the device is built with a single element sensor which is moved by translation slides or with 1D scanning over the area of interest) and generally by the system modular transfer function (MTF). As in any instrumental measurement, noise may appear on the imaging collected data. It may have different sources: one type that can be significant is generated by dark current that is the thermally generated charge in a CCD pixel that can be reduced by cooling. Moreover, there is a non-uniformity noise that comes from differential amount of dark current from each single element of the detector matrix. Linear pattern noise occurs due to leakage current and light across pixels and from pixels to serial registers and it is displayed as bright points or lines. The so-called read noise originates from the onboard pre-amplifier and it depends on the amount of signal that the system is designed to handle and of the readout speed. There are other sources of noise as the shot, the fixed-pattern, the thermal or the photon noise. All of them obviously depend on the characteristic of the IS device and they have to be individuated and considered in order to minimize them as much as it is possible [4, 25, 34].

Taking into consideration all the parameters that have just been presented, in the next section the imaging spectroscopy system used in this research work will be described. This device should?? have some advantages, disadvantages and potentialities in obtaining chemical information about cultural heritage objects that are directly correlated to its instrumental characteristics. For this reason, it is important to keep in mind the instrumentation possibilities in the imaging spectroscopy field, in order to understand the choices realized in the construction of this particular IS device and the feasible improvements that could be performed.

III.A.2 THE IMAGING SPECTROSCOPY SYSTEM

As it has been said before, the imaging spectroscopy system was developed and built by the Laboratory for Ultraviolet and X-ray Optical Research (LUXOR) of the IFN-CNR in collaboration with the department of Information Engineering DEI of the University of Padua. Without their collaboration, this work would not have been possible. The continuous teamwork between these expert engineers and the group of Chemistry of cultural heritage of the department of chemical science of the same university, in which this doctoral thesis has been developed, has permitted the constant improvement of the IS system. In some occasions, the confrontation has not been easy but it has always worked out and the results will demonstrate it, as it could be observed in the improvement of the spectra obtained from the first tests up to the application to the study of real artworks. The aim was to build a cost effective and robust portable system that operates mainly in the visible range with a high spatial and spectral resolution that could investigate *in situ* colouring agents, as instance. The imaging reconstruction capability of the device is significant but its potentialities to give information about the materials that compose the cultural heritage objects is more important for the purposes of this research work, and for this reason this aspect will be faced in many occasions during this chapter of the present doctoral dissertation.

The imaging equipment used for the acquisitions is constituted by three main elements: the imaging spectrograph, which can be considered the core section of the instrument, a rotation stage, over which the spectrograph is mounted, that permits the acquisition of large surfaces and the illumination system. All the components are controlled by a personal computer.

The imaging spectrograph consists of three main optical components, the objective, the dispersing element and the camera. In Figure III.1 , a scheme of the core section of the device is represented.

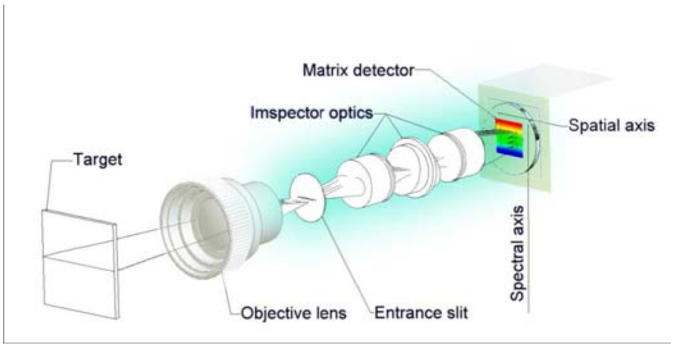


Figure III.3- Scheme of the imaging spectrograph, the core of the IS device

As it can be observed in this scheme, the objective lens focuses the image of the sample (target) to be acquired on the plane of the input slit of the spectrograph. The instrument measures the spectrum of the radiation that originates from the interaction between the light emitted from the illumination system and the materials that constitute the sample. In particular, it comes from a narrow rectangular region having width and height equal to the image of the entrance slit projected on the sample surface. To complete the 2D image, it is necessary to scan in the perpendicular direction to the slit height. The light coming from the rectangular narrow strip conjugated with the slit enters into the spectrograph, then it is dispersed by a dispersive element and focused on the plane of the 2D array detector. With reference to Figure III.1, the horizontal axis of the camera (parallel to the slit) is the spatial axis, while the vertical axis (perpendicular to the slit) is the spectral axis. This means that light coming from the same point (i.e. the same spatial position) on the sample but with different wavelengths is projected on the sensor on the same column but in different rows, that is in diverse spectral positions. On the other hand, light with the same wavelength (i.e. the equivalent spectral position) coming from different points of the object surfaces is focused on the sensor on the same row but in different columns (i.e. different spatial positions). A 2D spectral image can be recovered using a series of monochromatic images of a 2D region on the target obtained by scanning it in the direction perpendicular to the slit. In spectroscopy this operation is normally called rastering and its duration depends on the integration time of a single image and on the scanning speed of the mechanical pointing system of the instrument [8, 9].

The dispersive element that has been chosen to build the imaging spectroscopy device is the commercially available ImSpector V10 by Specimen [96]. It is a direct sight imaging spectrograph that can be quickly combined with a broad range of cameras. It can cover a broad spectral range over which it enables flexible wavelength selections via software. The ImSpector employs a direct sight on-axis optical configuration and a volume type holographic transmission grating. This grating is used in a prism-grating-prism construction (PGP element) which provides high diffraction efficiency and good spectral linearity. It is nearly free of geometrical aberrations due to the on-axis operation and independent of incoming light polarization due to the use of transmission optics only. The construction and operating principle of the direct-vision, dispersing PGP element will be briefly described. A collimated light beam is dispersed at the PGP and the central wavelength passes symmetrically through the grating and prisms (staying at the optical axis) and the shorter and longer wavelengths are dispersed up and down relative to the central wavelength. This working principle has many advantages when it is used in imaging spectroscopy instrumentation because it has a minimum deviation from the ideal on-axis condition and it minimizes geometrical aberrations both in spatial and spectral axis. In Figure III.2 the working principle of the PGP dispersing element [8, 9, 96] is reported.

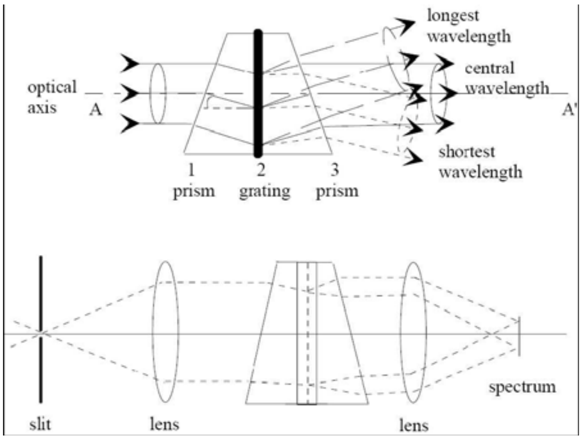


Figure III.2- Working principle of the PGP

The nominal spectral window of the spectrograph is from 400 to 1000 nm. The entrance slit size is 9.8mm x 25μm. Its dimensions define, together with the lens focal length and the distance from the lens to the object under observation, the length and width of the imaged scene line. There is no physical hole to the inner parts of the spectrograph and its glassy construction prevents dust particles to enter the actual slit surface. A special process is used to make both sides of the slit black in order to prevent reflections and reduce stray-light both in front of the slit and inside the spectrograph. The ImSpector has two high quality triplet lenses that are used to collimate light to the dispersing PGP element and to focus light to the detector surface. These lenses are designed for a wide field of view and a low f-number, and they provide excellent image quality by reducing several common aberrations. The PGP element uses a holographically produced transmission grating manufactured on DCG (DiChromated Gelatin) between two protective glass plates. Due to its characteristics (high diffraction efficiency, low stray light, no ghost lines), this material is commonly used to produce holographic optical elements [8, 9, 96].

The choice of the objective focal length is imposed by the required field-of-view (FOV) and spatial resolution in the direction parallel to the slit. Several objectives are currently available. A Computar f=16 mm, f/# 1.4, or a Canon f=25 mm, f/# 1.4, which both match the f/number of the spectrograph and were usually employed for the measurements whit the IS system.

In Table III.1 the most important technical specifications of the imaging spectrograph are summarized.

Table III. 1- Some technical characteristics of the Specimen ImSpector V10 Imaging Spectrograph

Specimen ImSpector V10 Imaging Spectrograph Specifications	
Spectral range	400-1000 nm
Numerical aperture	F/2.8
Slit width	25 μm
Slit length	9.8 mm

The sensor is a CCD camera Hamamatsu C8484-05G. It is a progressive scan interline CCD with micro-lenses, 1024 (spectral) X 1344 (spatial) pixel format, 6.45μm X 6.45 μm pixel size, 6.6mm X 8.7mm active area. The camera is moderately cooled to reduce the thermal noise and increase the sensitivity. The CCD has been successfully applied to scientific imaging and spectroscopy due to its notable ability to detect and quantify the light. The structure and basic applications of the CCD were developed at the AT&T Bell Lab in 1969 and from then on the technology has improved different factors, increasing its quantum efficiency, decreasing the amount of dark current and pixel size and reducing its costs. Ideally, a CCD chip consists of a pixel array that produces electrical charges proportional to the amount of light received at the different portions of this matrix. Each pixel has an intensity value and a spatial location. This value (counts as instance) represents the measured physical quantity, in this case the intensity of light reflected or transmitted by a sample. The sensitivity is determined by the quantum efficiency, which is the fraction of the incident photons that are converted to electrons in the wells of the CCD camera and by the read noise. The camera has 10 e^- rms (effective value of alternating voltage, expressed in electrons) readout noise, dynamic range of 1800:1 and quantum efficiency within the 0.35-0.70% range in the 400-750nm spectral interval as it can be seen in Figure III.3 [9, 25].

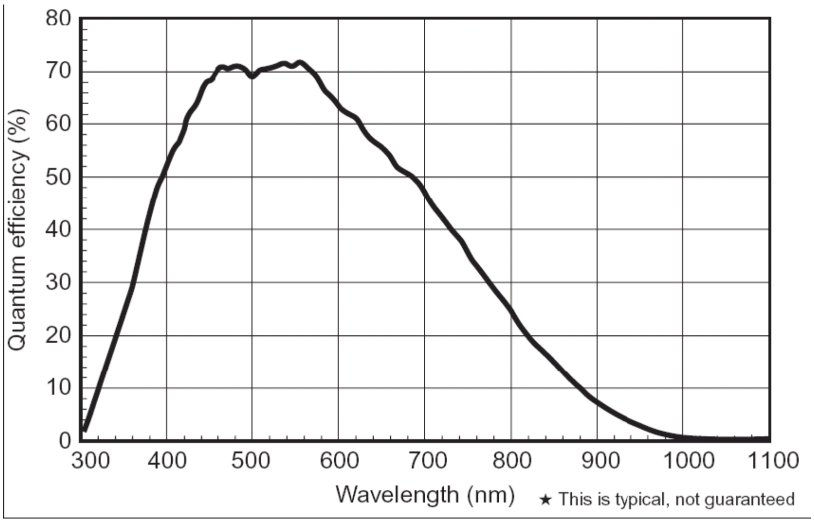


Figure III.3- Quantum efficiency of the CCD camera used as sensor of the IS system

The instantaneous field of view of the system in the direction parallel to the slit is limited by the number of pixels in the spatial direction. A spatial sampling of 2mm gives a field of view of 2.7m at a distance of about 5m with the f=16mm objective.

In Table III.2 some of the technical characteristics of the CCD camera used as sensor of the IS device are recapitulated.

Table III. 2- Some technical specifications of the CCD camera used as sensor of the IS system

Technical specifications of the Hamamatsu C8484-05G CCD camera	
Effective number of pixels	1344 (H) x 1024 (V)
Cell size	6.45 μm (H) x 6.45μm (V)
Effective area	8.67 mm (H) x 6.60 mm (V)
Readout noise (r.m.s.) (typ.)	10 electrons
A/D converter	12 bit
Exposure time	10 μs to 1 s
Lens mount	C-mount

Several solutions are possible to move the spectrograph in the direction perpendicular to the slit, so as to acquire a complete 2D image of the surface of the sample. The one that allows greater compactness when scanning large surfaces is a rotating stage. A linear translation of the instrument would require the construction of a frame that matches the dimension of the target; such a procedure is practically feasible only for small objects. The Physik Instrumente M-062 rotator was selected to build the imaging spectroscopy system. The scanning in the direction perpendicular to the slit is performed at constant angular steps. This means that the spatial pixel resolution increases with the incident angle between normal surface and scanning direction. However, in practice, the maximum incident angle does never get large enough for these variations to be significant. For example, working at a distance of 5 m, with an angular step of 0.5 mrad and performing 500 acquisitions symmetrically with respect to the normal surface, only a maximum incident angle of 125 mrad is reached. This means as instance a variation from 2.5 to 2.52 mm in the spatial pixel resolution [9].

The illumination system is composed by the emission source (or sources) of the radiation that interacts with the sample and subsequently arrives to the detector in order to be revealed as a visible spectra that can be interpreted with the purpose of obtaining information about the object composition. During the first measurements performed in this research work, different tests have been made in order to improve the acquisition methodology, including some regarding the illumination system. In this section, the final developed lighting setup will be commented. The light reflected by an object depends both on the object's characteristics and on the composition of the light illuminating the object. An ideal illumination source for the measurement of an object’s spectral reflectance (or trasmittance) should thus exhibit a uniform spectrum over the whole desired wavelength range. In the particular case of this IS device, the electromagnetic region of interest is the VIS and part of the NIR (400-1000nm). Unfortunately, an illumination apparatus that satisfies this condition over this wavelength range does not exist and, as a consequence, sub-optimal solutions must be adopted. State-of-the-art solutions for the imaging acquisitions of paintings mostly employ halogen lamps due to their smooth and broad spectrum. However, in the particular case of the built IS system, the combined effect of the low sensitivity of the CCD in the blue region and of the emission drop of the halogen lamps around those wavelength causes the signal to fall close to the noise. This consideration has suggested the necessity to use two different lamps, one with a broad, smooth spectrum covering the green-red region and one with a strong emission in the blue region [9].

Moreover, other considerations concerning the spectral emission of a lamp should be taken into account. When acquiring objects as those regarding the cultural heritage field, it is often unadvisable to employ lamps with a strong emission in the infrared spectrum as their heating may cause damages to the pictorial layer. The harmful effects that UV radiation can produce to some materials constituting a painting have already been commented. As the IS system was conceived for the acquisition of cultural heritage objects, a metallic iodide lamp was chosen to be used in the lower wavelength region due to its low emission both in the NIR and UV ranges [9].

The developed IS device has an illumination system that is composed of the following lamps:

- metallic iodide lamp of 70W or 250W (Disano)
- halogen lamp of 500W (Cixi Zhongfa)
- incandescence lamp of 100W (Osram)

These lamps are divergent directional sources. In Figure III.4 on next page, the emission spectra of them are showed. They have been measured by acquiring a white target of known reflectance illuminated by each source. The graphs represent the spectral power density of the emission sources, expressed in CCD counts. In the particular case of the metallic iodide lamp, the camera exposure time and the shutter aperture was set in order to have a strong signal in the blue region where this source emission intends to be employed. This has provoked a saturation of the signal in the interval between 530nm and 680nm (see Figure III.4(a)). However this fact does not affect the spectra obtained because this spectral window will not be used as it will be clarified consecutively. A zoom of the emission spectrum of the metallic iodide lamps in the blue region can be observed in Figure III.4(b) [9].

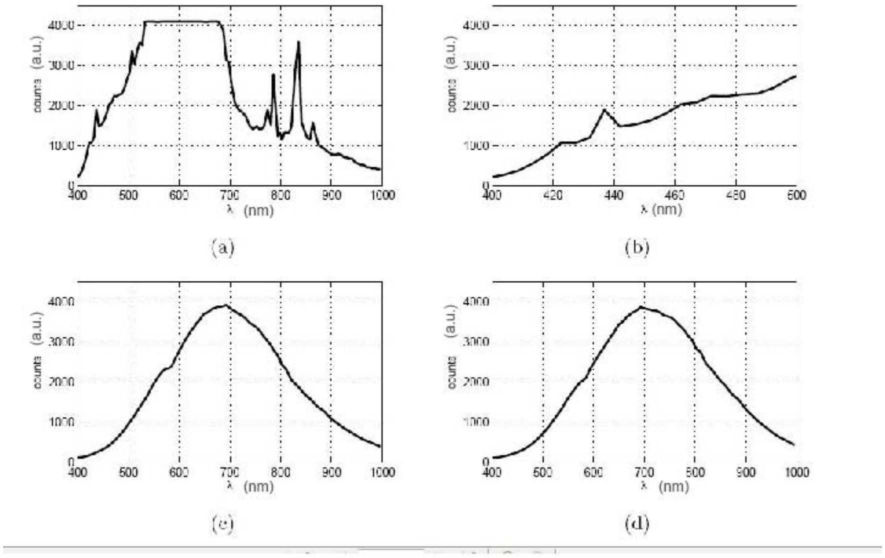


Figure III.4- Emission spectra of the three lamps used in the illumination system of the IS system:
(a) metallic iodidelamp (b) metallic iodide lamp (blue region) (c) halogen lamp (d) incandescence lamp

As it can be seen in Figure III.4 (c)-(d), the spectral power densities of the halogen and incandescence lamps are almost identical with the bell shape and shifted towards the red region with respect to the metallic iodide lamp. Their use is practically interchangeable and tied to the particular environment of the acquisition: for the study of large surfaces, as when analysing a mural painting, the halogen lamp may be preferred due to its higher power and wider illumination area, while for laboratory tests or the acquisitions of small paintings it may be overpowered and the incandescence lamp may result more convenient. In the case of the metal iodide source, two different powers are available, 70W for relatively small samples that require a narrower illumination area than a large-sized object that needs a more powerful emission source furnished by the 250W.

The illumination setup of the IS device is composed by the metallic iodide lamp (250 W Powerstar HQI-TS 250W/NDL and Powerstar 70 W HQI-TS 70W/NDL), and the incandescence (100W Osram) or halogen (500W Cixi Zhongfa Lamps Co.) lamp utilized in sequence. The spectra have been obtained by juxtaposing at 500nm the signal intensity measured with the metallic iodide lamp in the blue region to that obtained with the halogen/incandescence lamp in the long wavelength interval. When using these combined setups, a scaling has been performed in order to eliminate the discontinuity between the reflectance acquired with the metallic iodide lamp and that measured with the other lamp. This scaling is often performed when measuring reflectance spectra with other well established devices, therefore the corresponding performance characterization results are meaningful. The number and power of the lamps employed will depend on the size of the cultural heritage object under consideration. The benefit of the use of an illumination system with such characteristics is the combination of versatility to be applied to different analytical issues with portability that allows *in situ e*xaminations [9].

The different components of the IS device are controlled from a computer. For the spectral image analysis, Matlab routines and environment are used in order to process the data collected and to obtain the digital image reconstructions, the chromatic coordinates and the visible spectrum of the regions of interest of the sample under consideration.

It should be mentioned that this IS device is easily integrated with other scanning instruments, for example a time-of-flight laser scanner acquiring 3D information. In these conditions, the developed system can measure the shape and the colour, which can be an astonishing feature when studying cultural heritage objects that are not planar as polychromatic statues or painted vaults [9].

Afterwards, some performances of the instrument have been verified before starting any sample measurement (instrument characterisation). The spectral calibration of an imaging spectrograph consists in determining the correspondence between pixel indexes and wavelengths. The calibration has been performed by measuring the spectra of low pressure gas lamps (such as Hg, Cd, Zn, He or Kr lamps) which emit very narrow spectral lines characteristic of the element in the lamp. The correspondence between pixels and wavelengths has been found to be nearly linear. With respect to the 16 mm objective, the spectral dispersion is 72.1 nm/mm and the spectral resolving element is 0.465 nm/pixel. On the other hand, for a focal length of 25 mm, the spectral dispersion and the spectral resolving element are respectively 70.2 nm/mm and 0.453 nm/pixel [9]. Calibration with respect to intensity linearity is evaluated by acquiring eight standard grey tiles by Labsphere [97], which cover an intensity ratio of 50:1. The measured spectra are almost constant and in very good agreement with the calibrated ones. The response of the developed system was also evaluated by acquiring the reflectance spectra of eight Labsphere coloured calibrated tiles. The data obtained by the IS device has qualitatively matched with the reference curves [8, 9]. The characterization of the instrument with respect to the spatial resolution can be performed through the use of a parameter called Contrast Transfer Function (CTF), which gives the minimum detail that can be distinguished on the sample. The CTF is evaluated by measuring the contrast C of a calibration image featuring a set of black and white lines with an increasing spatial frequency. The minimum detail that can distinguished on the target depends on the size of the spatial resolving element, which in turn depends on the sample-IS device distance and on the objective focal length. It has to be reminded that the actual CTF is limited by the camera pixel size projected on the sample surface and this means that the optical aberrations of the whole system (objective-spectrograph-camera) are negligible. It must be considered that the analysed objects can show irregularities on the surface, usually they are not perfectly flat because as instance a painter would fancy some “texture” in his artwork surface or leave the signs of the brushes. If the depth of field of the instrument is not sufficient, there could be problems with the final results of the acquisitions. All elements in the object surface are precisely focused in the image plane, disregarding lens aberrations. However, objects both closer to and farther from the lens send bundles of rays that focus farther from and closer to the image plane, respectively. Thus a flat film, situated at the image plane, intercepts circles of confusion corresponding to such object points. If the diameters of these circles are small enough, the resultant image is still acceptable. The depth of field is then said to be the interval in object space between two points whose images lie within the maximum diameter of the circle of confusion. At a distance of 80 cm, the depth of field of the instrument is about 10 cm, more than enough with respect to a large variety of coloured cultural heritage objects as paintings or mosaics [8, 9, 97].

At this point, the developed Imaging Spectroscopy system seems ready to be applied to the study of the visible spectra of samples of interest for the field of cultural heritage. In Figure III.5 on the next page, a picture of the IS transportable device during the *in situ* analysis of a painting performed on November 2010 is shown. The image illustrates an overview of the instrument but it can be noted that it is relatively compact and transportable.

Figure III.5- The developed IS device during an *in situ* analysis of a painting

III.B Development of a VIS reflectance measurement methodology by the IS device

Previously the IS device has been described from the instrumental point of view. Different performances of the instrument were verified using calibrated materials and from the result observed during this characterisation operations it could be concluded that the IS system was ready to perform reflectance spectra analysis on “real” samples.

The initial choice was to analyse a fragment of a mosaic composed by different coloured *tesserae* in order to study the chromophores employed in them and introduce the IS technique to the study of glass materials. Unfortunately, the results obtained were disappointing and this had provoked a change in the procedure of the research work to this necessary step: the development of a visible reflectance measurement methodology with the IS device. This part can be considered the core of this doctoral dissertation and is also the harder part to structure because many problems and issues have been overcame, always in a constant collaboration with the engineering research groups of the LUXOR and the DEI. For the sake of clarity, before starting with the discussion of the different parts that integrate this section, a table will summarize the most important points of the procedure adopted to have a clear perspective of the evolution, problems, improvements.. The Table III.3 on next page recapitulates the structure that will be follow in this doctoral to present the workflow of the employed methodology.

Table III.3 – Structure followed in this doctoral dissertation to present the employed workflow during the development of a visible reflectance measurement methodology through the IS system

SECTION	SAMPLES IMPLIED	AIM	PROCEDURE	RESULTS/OBSERVATIONS/CONCLUSIONS
III.B.1 FIRST TESTS	Mosaic fragment M	Study the possible applications of the IS device to characterize chromophore of glass *tesserae*	Comparison the visible reflectance spectra obtained by the IS device with the ones collected by commercial spectrophotometers	- Data obtained with the IS device not in good correspondence with the information collected with the well-established spectrophotometers: spectra acquired meaningless and with spectral features not due to the materials under analysis - Necessity to improve the acquisition setup and illumination system: different tests to individuate the best methodology - Requirement of more simple samples to verify some aspects due to the relative mosaic fragment complexity
III.B.2 COMPRESSED PELLETS OF COLOURED PIGMENTS	Powder of pure pigments compressed in pellet form	Validate the reliability of the IS system and verify the useful wavelength range and spectral resolution	Acquired the VIS reflectance spectra of the coloured samples with the IS device and compared the results with references and the data collected with other well established instrument	- IS VIS reflectance spectra in good correspondence with the references and with the information furnished by other instruments - Discrimination of the useful wavelength range and an adequate spectral resolution
III.B.3 STUDY OF SIMPLE LABORATORY PAINT FILMS DURING AN ACCELERATED AGEING PROCESS	Paint film composed by powder of green pigments dispersed in linseed oil medium deposited in glass prepared in laboratory	Verification of the reliability of the IS device. Test its analytical power to detect optical changes during and artificial ageing process and mapping skills	Acquired the VIS reflectance spectra of the paint films at different steps of an artificial ageing process with the IS device and compared the results with references and the data collected with a spectrophotometer	- IS system was able to detect the optical changes suffered by the paint films during the artificial ageing process - Ability to characterize, to differentiate, to map and to monitor painting materials - Improvement of the Signal/Noise: compromise between spatial resolution and the quality of the visible reflectance spectra obtained by the system
III.B.4 CALIBRATION PROCEDURE	Various references Labsphere tile, white paper, laboratory paint films and a mural painting	Improve the IS system performances through a better calibration procedure to obtain more robust data	Test different calibration procedures that include the use of different materials and measurements with the IS device and benchtop spectrophotometer.	- IS device shows some problems when dealing with some materials of high reflectance. However it not seems to be a critical issue - Calibration procedure employed adequate. Nevertheless, it could be additionally improved
III.B.5 IMPROVED MEASUREMENT SETUP AND PROCEDURE	→ Measurement procedure. Final Acquisition Setup and summary of the IS system characteristics			

III.B.1 FIRST TESTS

As it has been said previously, the developed IS device was firstly applied to the study of the chromophores of the coloured glass *tesserae* of a fragment of Mosaic of the *Basilica di San Marco* in Venice. Such data are important to chemically characterise the vitreous materials, to classify in diverse groups the diverse glass fragments and to obtain information about the technology of production of such kind of objects. The aim was to compare the IS response with the one obtained through a Fiber Optics Reflectance Spectrophotometer to verify it. The chemical characterisation of such kind of cultural heritage artefacts could represent an interesting application field for the IS device because they usually cover large-sized areas so the imaging spectroscopy technique can be advantageous if compared with a spot technique as FORS because it collects information saving time.

UV-VIS-NIR reflectance spectroscopy has been already applied to the study of chromophores in mosaic *tesserae* [98, 99]. However, the methods used are generally spot techniques as FORS and to the authors knowledge IS has not been applied to the analysis of such kind of objects. For this reason such application field seems challenging.

The fragment of mosaic that has been studied was nominated sample M. It comes from the *Battistero* of the *Basilica di San Marco* in Venice (Italy) and it is dated back to 1340. The building is characterised by marvellous glass mosaics covering all the walls and the ceiling of the church. It is a small piece of glass mosaic which measures approximately 11cm x 8cm x 3cm. It is constituted by 65(M1-M65) coloured *tesserae*, which are linearly disposed in order to reproduce the aspect of some kind of object that cannot be recognized. The back of the sample shows the original mortar and the straw used in its preparation. In Figure III.6 on next page a picture of the fragment of mosaic M is showed together with the numeration adopted for each glass *tessera* [100].

The sample was already studied by the Mobile laboratory MOLAB research group of the *Università degli studi di Perugia* (Italy) with different techniques, including analysis by UV-Vis spectroscopy with a FORS instrument (see Annex 1) in the wavelength range from 250nm to 1000nm. The obtained spectra of the coloured *tesserae* could serve as a “reference” to control the reliability of the results acquired by the IS device.

Figure III.6- The mosaic fragment M (left) and the numeration of the glass *tesserae* adopted (right)

The Imaging Spectroscopy system has been employed to study the sample M. In one measurement, the device is able to collect the visible reflectance spectra of all the pieces of glass. Despite the fact that the instrument has been previously characterized, the results were absolutely disappointing. Several attempts were made to verify that it was not due to a sporadic error or a consequence of some kind of mistake during the acquisition procedure but all the tries lead to similar unsatisfactory results. In Figure III.7 the digital image reconstruction of the mosaic M obtained from one of these essays is illustrated. As it can be seen on this picture, the two upper blue glass *tesserae* M1 and M2 were separated from the sample for practical reasons. In this RGB reconstruction it is possible to select the regions of interest and study their reflectance spectra. The spectra obtained were not in agreement with the ones obtained with the FORS technique. Some examples of these acquisitions will be showed and compared with the MOLAB results. It must be taken into account that the two methodologies use different acquisition systems with diverse illumination, geometry… and as a consequence some differences were expected, but this did not justify the kind of spectra obtained in these measurements.

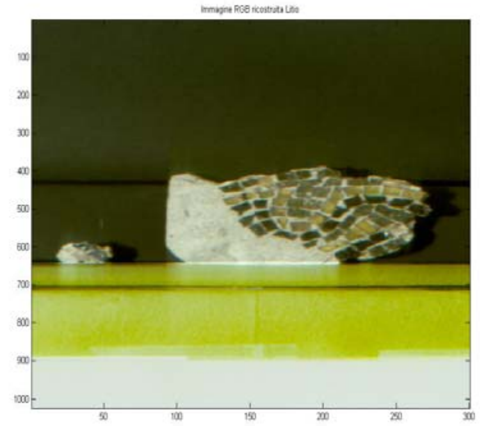


Figure III.7- Digital RGB reconstruction of the mosaic fragment M and the blue *tesserae* M1 and M2 on the left

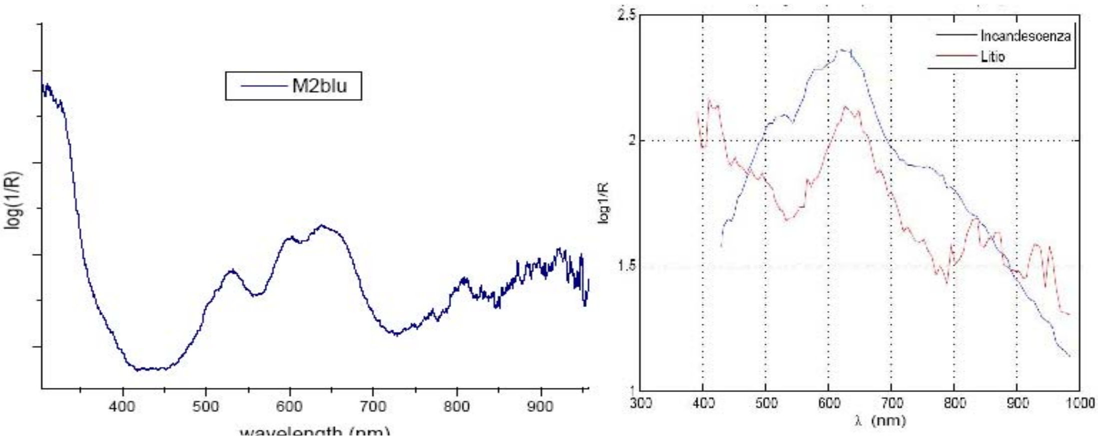


Figure III.8- UV-Vis-NIR Reflectance Spectra obtained by means of FORS (left) and of the IS system (right) of the blue tesserae M2

In Figure III.8, a comparison of the results of the analysis performed on the blue glass *tesserae* M2 obtained with the IS device and by the MOLAB laboratory is showed. The FORS curve have some features bands (due to Co(II) as instance) that are not present in the IS spectra. It must be specified that the data showed are some of the best that have been collected during different attempts. It was really discouraging to acquire repeated times such kind of results which are generally noisy, meaningless, difficult to interpret or in some cases they could lead to erroneous conclusions. It can be observed from the comparison in Figure III.8 that a few spectral features are presented in the curves collected with both instruments, as the absorption band at near 600nm but in the other hand there are parts of the spectra acquired with the IS system that have a behaviour that is “opposed” or not in good agreement to the ones obtained with the well-established FORS instrumentation as the shape of the reflectance curve in the upper wavelengths (in the NIR range). In fact, as a general conclusion of these results, it can be said that many of the spectra collected by the developed device show in the NIR region a behaviour in opposition with the ones acquired by the MOLAB laboratory. In repeated occasions, the IS system records in this part of the spectrum decreasing curves while the FORS data display a quite increasing behaviour. It was hypothesized that this could be due to the loss of efficiency of the detector in this region and to the acquisition setup, in particular to the illumination system. For this reason, some tests were performed, trying different lamps, as it has been anticipated in the description of the instrument and that would be commented soon. As it can be observed, in the graphic representing the data collected by the IS device, there are two curves, one blue and one red. They correspond respectively to the information acquired employing an illumination system based in the use of an incandescence lamp alone (blue) and of a single metal iodide lamp (red). In Figure III.9, another comparison of the results obtained with the IS device and by the MOLAB laboratory is showed. It is possible to observe that the quality of the information collected is similar. In this case, the spectra correspond to the green glass *tesserae* M4.

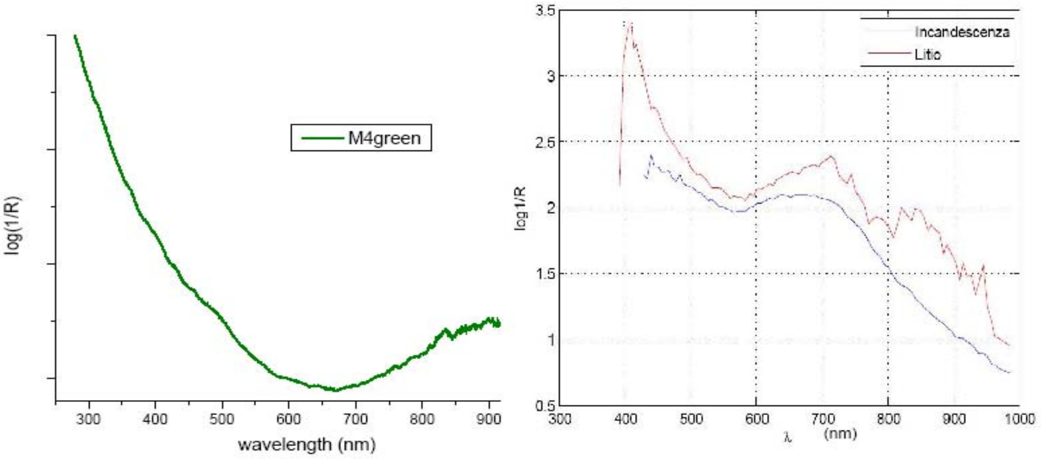


Figure III.9- UV-Vis-NIR Reflectance Spectra obtained by means of FORS (left) and of the IS system (right) of the green tesserae M4

Due to the disappointing results obtained, it was obvious that some aspects of the IS device must be optimized. As it has been previously affirmed, different experiments regarding diverse illumination choices (in terms of lamps and geometry) had been tested. Several attempts were performed using the metallic iodide, the incandescence and the halogen lighting alone. Then, numerous essays were tried with these lamps together, that means contemporarily with identical exposition times, or using the metallic iodide one in a sequence with the incandescence or the halogen emission sources. In this last conditions, the exposure time can be diverse for each lamp which is an advantage because the requirements for each of them can be different. Different electrical powers were tried too. The geometry was changed also during the different experiments placing the sources at approximately 45°/0°/45° or at almost 45°/0°. It seemed that the best solution was the employment of the metallic iodide lamp in sequence with the incandescence or the halogen emission source. However, in some of the experiments perform to optimize this sequenced illuminating system they have been additional problems. In some of the collected spectra it can be observed that they are some signals that are not due to the analysed materials. In Figure III.10 a spectrum of a red tile used in the optimizing experiments where one of this “spectral feature” was appeared and it is not due to the composition of the material. It has been hypothesized that these spectral features are a consequence of the setup employed, in particular to the illumination system. For this reason, the employment of some filters in conjunction with the lamps that had been listed before were also tested in order to verify if its use could contribute to improve the illumination system including the elimination of these fake signals too.

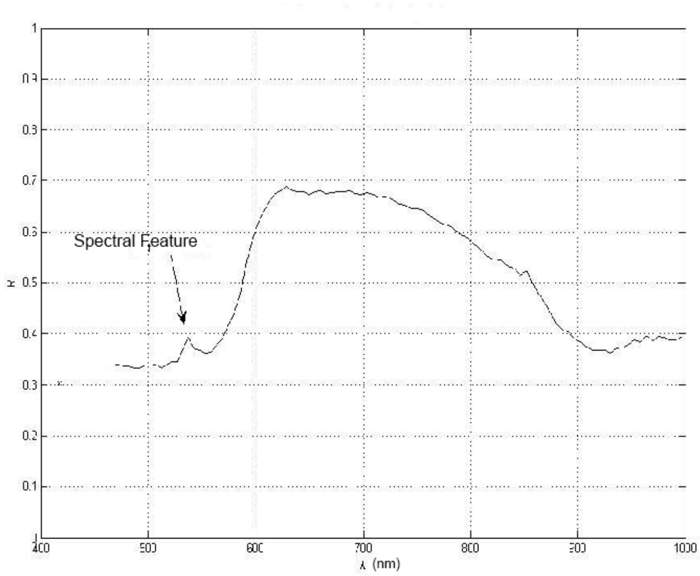


Figure III.10- Spectral Feature in one of the spectrum collected with the IS system

After these tests, the acquisition setup was optimized, in particular from the point of view of the illuminating system. As it has been commented in the description of the IS device, for the analysis of relatively small objects in laboratory as instance, the use of a metallic iodide lamp of 70W in a sequence with a 100W incandescence bulb juxtaposing the reflectance spectra at 500nm. The geometry employed is 45°/0° in order to avoid specular reflectance and usually one emission source each time (which means to execute first the measurement with the incandescence bulb and then with the metallic iodide lamp or vice versa) is sufficient to homogeneously illuminate this kind of sample. For large-sized objects, as a mural painting, the more adequate lighting conditions are the employment in sequence of a 250W metallic iodide lamp (or lamps) with a 500W halogen emission source (or sources) juxtaposing the reflectance spectra at 500nm. The setup adopted has a geometry of approximately 45°/0°/45° because, in order to homogenously illuminate the large-sized surface, two lamps per measurement are required although in some cases the 45°/0° is sufficient. These individuated illumination conditions seem to give the best results in terms of coherence of the reflectance spectra collected, of safety for the cultural heritage objects and of the intensity of the signal detected. The spectral features were a consequence of the metallic iodide lamp in some conditions of exposure time/signal saturation but with the methodology adopted they disappeared. However, in the next phases of the work the behaviour of the data collected has been monitored taking particular attention to the signals with the same characteristics. Other aspects of the acquisition procedure regarding the software operations were changed during these first tests as the gain regime of the detector.

Thanks to this phase of the work, some aspects regarding the acquisition of reflectance spectra with the IS system were improved. However, it was also evident that some issues found during these experiments needed further research. In particular, from the spectral data obtained, it was possible to observe a non reliable behaviour in the extremes of the wavelength range. It has been hypothesized that this was provoked in part to the illumination system but also to the quantum efficiency of the detector. The next step was planned n order to verify the reliability of the IS device after the improvements individuated, to identify the wavelength range where the response of the instrument is consistent and robust and to recognize the adequate spectral resolution to obtain spectra of sufficient quality but at the same time adequate to be handle and processed via software. To differentiate these important parameters, the mosaic fragment M is a sample too complex to be used as a test material to individuate these significant characteristics. In fact, this object can be interesting to study the application field when all the improvement operations will be performed but its acquisition present some problems as specular reflection due to the presence of golden leaf glass *tesserae* and a generally low spectral reflectance signal of the coloured glasses. For this reason, to develop the next section another samples were specially prepared to reach the aims of this part of the research work.

III.B.2 COMPRESSED PELLETS OF COLOURED PIGMENTS

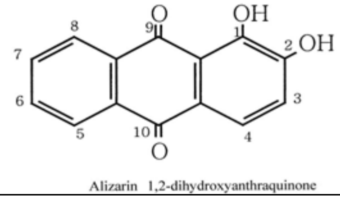
III.B.2.A Purposes and Methodology

The purposes of this section are: 1) to define the wavelength range were the response of the IS device is robust and 2) its spectral resolution. The nominal range where the CCD sensor and the spectrograph work is between 400-1000nm but it is possible that the spectral window where the system is reliable could be narrower and it is important to verify this characteristic of the IS system because its power as an analytical tool will be deeply influenced of the effective wavelength range. It is also important to discriminate a satisfactory spectral resolution that allows to obtain reflectance spectra of quality to be elucidated but at the same time avoid the acquisition of imaging data cube to much difficult to handle. In order to reach these aims, it was decided that the best choice was to prepared samples composed only by pure coloured pigments and study them by means of the IS system and of a benchtop spectrophotometer (Varian Cary 5000, see Annex 1). It must be taken into account that both instruments are different in terms of illumination or viewing geometry and some difference (error) can be tolerated between the data collected with the two apparatus. However, in order to accept the IS procedure, the information must be in good agreement and special attention will be taken to the shape of the spectra, most concretely to the absorption bands that the technique under discussion is able to discriminated.

III.B.2.B Samples

To reach the aims of this phase of the research work, five pellets were prepared by compression of powder of pure pigments. The colourants were selected in order to have spectral features in the range from 400-1000nm. The materials were acquired from commercial sources, in particular from Kremer Pigmente [101]. Violet, blue, green, yellow and red pure pigments were chosen in order to cover the wavelength range. The employment of more colours seemed unnecessary. In order to handle with more facility the pigments, it was decided to use them in form of pellets. A manual hydraulic press and an evacuable pellet die of 13mm of diameter (which normally are used in the elaboration of the IR sample in KBr pellets) were used to press the powder with a maximum load of 10 tons. The colouring powders have different tendency to aggregate and for this reason some pellets were less resistant from the mechanical point of view. In Table III.4 (next page) the pigments selected are enumerated and in Figure III.11 (next page) a picture of the prepared samples is shown. In the particular cases of Ultramarine blue and of the Manganese violet it was more difficult than in the other cases, obtaining delicate samples that had to be carefully handle. In the case of Chromium(III) oxide, the pellet was resistant but during a measurement test it has been accidentally broken, as it can be seen in Figure III.11, but the sample still remained of enough size and quality to perform the analysis.

Table III. 4- Pigments employed to prepare the pellet samples and some of its characteristic [38, 73-76, 101, 102].

Pigment	Chemical Composition	Characteristic	Spectral Features
Alizarin Crimson Kremer	 Alizarin 1,2-dihydroxyanthraquinone	Red lake pigment used since antiquity times extracted from some plants roots	$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions leading to a strong sharp increases in the reflectance curve at ~600nm
Italian Gold ochre light Kremer	Natural yellow ochre found in Italy, mainly colouring agents goethite α-FeOOH	Natural ochre pigments are used since antiquity times	Ligand to metal charge transfer and transition due to a d^5 configuration in high spin O_h environment
Chrome Oxide green Kremer	Chromium (III) oxide Cr_2O_3	Green pigment synthesized since the 19th century	d^3 configuration leading to two strong absorption bands in the visible
Ultramarine Blue synthetic Kremer	Sodium-aluminium-sulfo-silicate ~ $(Na,Ca)_8[(Al,Si)_{12}O_{24}](S,SO_4)$	Blue synthetic mineral pigment inspired from the natural pigment Lapis Lazuli obtained from the semi-precious stone	Charge transfer transition that leads to a strong absorption band centred at ~600nm
Manganese Violet Kremer	Manganese (III) Ammonium Pyrophosphate $NH_4MnP_2O_7$	Violet synthetic mineral pigment invented by Leykhuf in 1868	Absorption broad band of Mn(III) at ~540nm

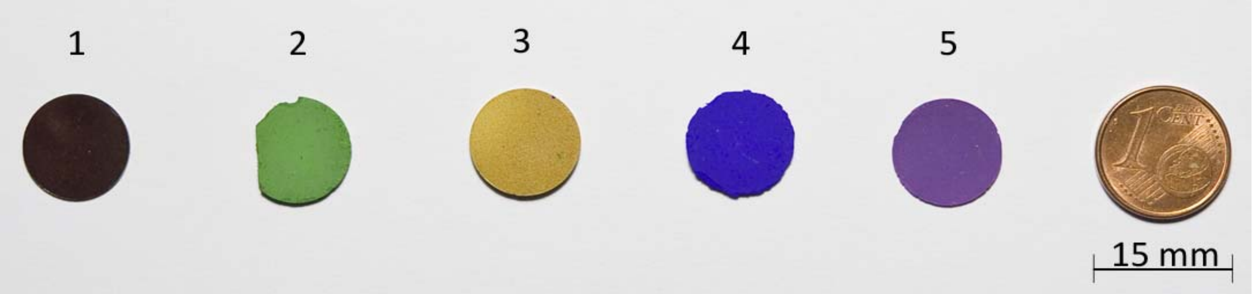


Figure III.11- Samples prepared, pellets of pure pigments from Kremer pigmente [101]: (1) Alizarin crimson (2) Chrome oxide green (3) Italian gold ochre (4) Ultramarine Blue (5) Manganese Violet

III.B.2.C Results and discussion

The samples were analysed by the IS system and by the benchtop spectrophotometer Cary 5000. The spectra obtained with both instrument were compared between them and with the information that could be collected from different references. Despite that the nominal wavelength range of the CCD detector and of the imaging spectrograph (from 400-1000nm), it has been verified during the measurement of these simple coloured samples that the interval were the IS system is reliable and robust is from 420 nm to 850nm, which is mainly the visible range and a small portion of the NIR. The system is not reliable in the extremes of the interval because the CCD quantum efficiency is minor at the ends of the spectral window and at the same time the signal in those region is lower due to a lower emission of the illumination sources. The causes are the same but they influenced in a different manner. In the UV limit (400-420), the cause of the non reliability of the system is principally due to the illumination system. In fact, the quantum efficiency of the detector (that can be observed Figure III.3) is lower than in the central part of the spectral window but it is still above the 50%. In this part of the spectrum, the emission of the source is more critical than the quantum efficiency. The use of the metallic iodide lamp from 400nm to 500nm was adopted to improve the illumination conditions due to the small emission in this fraction of the incandescence or halogen lamps. This solution was satisfactory but at the same time has the drawback that the emission spectra of this source (Figure III.4 (a) and (b)) is not "continuous" but it is characterized by "peaks". Due to all these factors together, the first reliable point for the developed IS system in the lower wavelength limit is at 420nm. In the other hand, in the upper wavelengths, the critical factor is the loss of quantum efficiency (see Figure III.3) which is minor of the 50% from 700nm to longer wavelengths. This fact together with the decreasing of the intensity of the emission sources employed (Figure III.4 (c) and (d)) has as a consequence that from 850nm to the NIR frequencies the system is no longer consistent.

The other important fact that should be determined was the spectral resolution. It has been observed that collecting 82 spectral bands , corresponding to 82 images to form the hyperspectral cube (remember from chapter I that hyperspectral is used for more than ten or twenty) lead to reflectance spectra of enough quality. This corresponds to an average spectral resolution of approximately 5.4nm (430nm/82=5.2nm) that seems sufficient to interpret the features of the electronic spectra in the wavelength range of interest. In fact, the visible features usually are broad and not narrow. From the experiments performed it has been verified that the 82 layers of the hyperspectral spectroscopic image data cube can be stored and processed easily by the specially developed Matlab routine and leads to reflectance spectra that allow to observe its characteristic absorption bands.

The reliability of the individuated wavelength range of work and the suitability of the spectral resolution attained will be show through the spectra obtained from the analysis of the pellet samples composed of pure pigments. The results will be illustrated comparing the reflectance curves collected by the IS device and by the spectrophotometer in the same graphic divided by pigment. It will be observed the good correspondence between both measuring system in the interval from 420nm to 850nm and the convenience of the spectral resolution of the developed IS system.

- Alizarin Crimson

In Figure III.12 the spectra collected for the pellet formed by the pigment alizarin crimson with the IS device and with the spectrophotometer are showed.

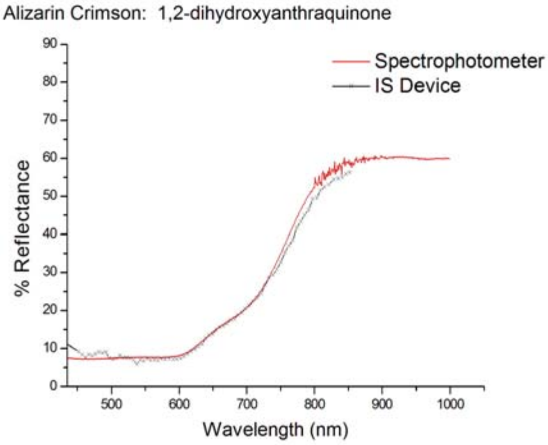


Figure III.12- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the pellet of the Alizarin Crimson

As it can be observed, the results given by the IS device are in good agreements with the ones recorded by the spectrophotometer. The reflectance curves are also in correspondence with the information found in the references. The chromatic properties of this class of molecules depend on the position and number of the hydroxyl-substituents. The absorption behaviour in the visible region of these antraquinones based dyes is principally due to the n $\rightarrow$ π* transitions of the carbonyl groups and a π $\rightarrow$ π* UV intense absorption band that occurs under 350nm. The strong absorption band arise at approximately 500-560nm with a shoulder at nearly 490nm given a reflectance peak at about 420nm and a strong a sharp increase in the reflectance curve at about 600nm [10, 11].

- Yellow Ochre

The main feature of the spectrum of pure goethite is due to a ligand to metal charge transfer transition that can be observed as an strong increase in the reflectance at about 500nm (with an inflection point at approximately 550nm). There are other absorption bands at approximately

649nm, 480nm and at 434nm of the Fe(III) which presents a d^5 configuration in high spin in an octahedral environment (O_h). These characteristics are very weak because this ligand field transitions are bounded to more strict selection rules (Laporte and Spin selection rules) [103].

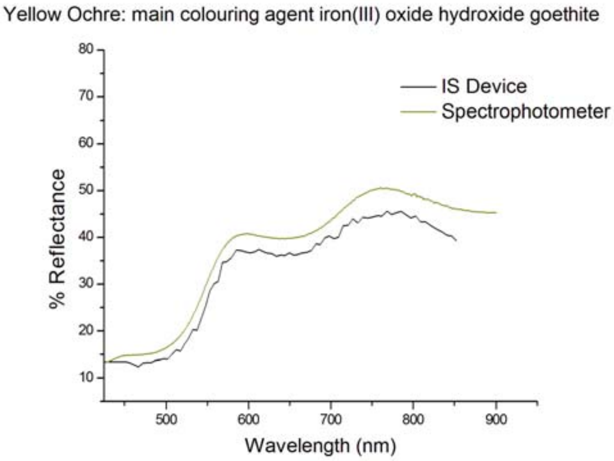


Figure III.13- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the pellet of the yellow ochre

In Figure III.13, the spectra obtained by both instrument are illustrated. As it can be observed, the IS system furnished information which matched with the data obtained by the spectrophotometer. The spectral curves have the characteristics described in the references. It can be also noticed that the IS reflectance spectrum has a signal to noise ratio worst than the one recorded by the spectrophotometer. However, it can be affirmed that in the range from 420nm to 850nm, the results are satisfactory and the main spectral features in the visible region for this pigment can be discern.

- Chromium (III) oxide

The principal transitions in the Cr_2O_3 are due to the Cr(III) in an octahedral environment. In Figure III.14, the spectra obtained with both reflectance measurement system are displayed. It can be seen that despite the fact that the IS spectrum is noisy, the results are generally in good agreement. The complex compounds of Cr(III) has a d^3 configuration and they showed at least two well defined bands in the visible region due to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$. These strong absorptions can be noticed in the spectra collected as minimum in the reflectance at approximately 460nm and 600nm [77].

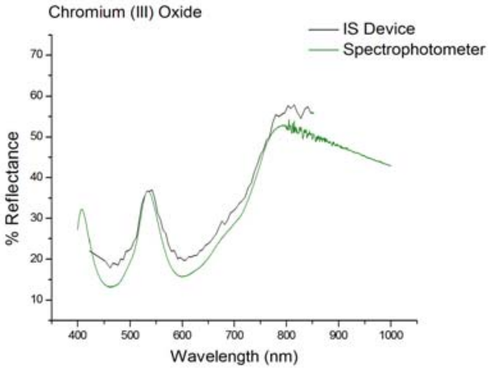


Figure III.14- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the pellet of the chromium (III) oxide

- Ultramarine Blue

The visible spectrum of this blue is characterized by a strong and broad absorption band centred at 600nm as it can be observed in Figure III.15.

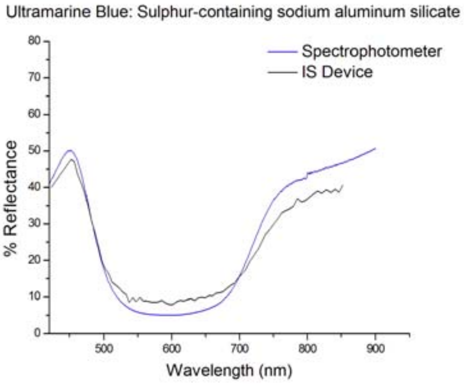


Figure III.15- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the pellet of the ultramarine blue pigment

As in the precedent cases, the results obtained with both system are in good agreement. The IS system furnishes reflectance curves more noisy but this do not impede the detection of the strong absorption band at about 600nm due to the charge transfer transition in the S_3^- group presents in the lattice structure of the aluminium silicate [17].

- Manganese Violet

The results obtained with both measurement systems are in good agreement as it can be seen in Figure III.16.

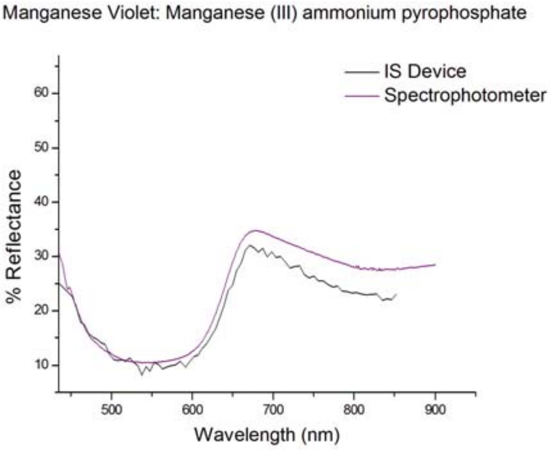


Figure III.16- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the pellet of the manganese violet

As for the previous samples, the IS device collects reflectance information which is noisy if compared with the spectrophotometer but despite this fact the spectral features are recognizable. In this case, the colour is produced by the Mn(III) which produce a broad band at about 540nm.

III.B.2.D Conclusions

The experiments conducted on the samples prepared with pure pigment (alizarin crimson, yellow ochre, chrome oxide, ultramarine blue and manganese violet) had permitted the individuation of the wavelength range were the IS system is reliable. The response of the developed device is consistent between 420nm and 850nm as it can be observed from the spectra obtained and that had been showed. This spectral range is relatively narrow and it mainly includes the visible region. However, it could be useful in the characterisation of pigments and as a constituent of a multi-technical approach to study *in situ* cultural heritage objects. Reflectance spectra on the visible range was already used for this purpose [18, 22, 104] and also imaging spectroscopy in some specific cases [22]. Anyway, the usefulness, potentialities and limits of the developed IS system will be demonstrated with some results in further sections of this doctoral dissertation. The recognition of the wavelength interval were the system acquires reliable spectra has been a key step of the research work. It is essential to delimitateidentify this range in order to understand the applications were the instrument could be useful and also to verify its suitability to perform reflectance measurement and individuate potential factors that can be improved. After the disappointing and not much significant results collected in the precedent part, the data acquired during these experiments were quite encouraging. The spectral resolution, of approximately

5.2nm (average), seems adequate taking into account the detected absorption characteristics of the pure pigments observed in the spectra obtained from the pellet samples. On the other hand, the reflectance curves procured by the IS device are noisy if compared with the ones gathered by the spectrophotometer. It should be investigated if the results can be improved from this point of view. More tests to verify the significance of the data furnished by the developed system are required together with further verifications of the reliability and quality of the attained spectra in the individuated range from 420nm to 850nm. Furthermore, additional experiments must be perform to understand its potentialities in the characterization of pigments as instance. These aspects will be subsequently treated in the following section that deals with the next step in the development of the VIS reflectance measurement methodology with the built IS device.

III.B.3 STUDY OF LABORATORY PAINT FILMS DURING AN ACCELERATED AGEING PROCESS

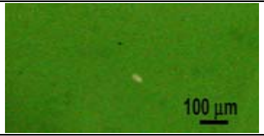
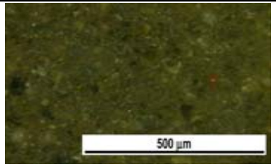
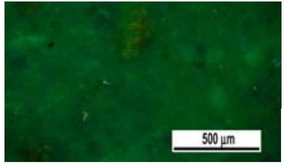
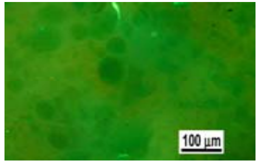
III.B.3.A Purposes and general methodology

After the definition of the wavelength range between 420-850nm with a spectral average resolution 5.2nm where the system seems robust, it has been decided to study samples a little more complexes, from the point of view of the materials employed and from the methodology. The specially prepared systems were composed basically by a pigment dispersed in a binding medium and were exposed to an artificial accelerated ageing process. The purposes of these experiments were to produce optical changes in the samples provoked by the ageing and to test if the IS system was sensible enough to detect such alterations on the laboratory prepared paint layers. The pigments employed to made the “replicas” were selected of the same colour in order to examine in contemporary the capacity of the system to differentiate and characterize the colouring agents in paint layers. So, there were different aims in this phase of the research work. Firstly, the analytical skills of the IS device to detect optical changes during an accelerated ageing process was tested. The process was executed in steps, and at the different phases the samples were analysed by the IS system and with a benchtop spectrophotometer (Varian Cary 5 and Cary 5000, see Annex 1) in order to verify the consistence of the data. This procedure allows not only to observe the changes during the ageing process but also to verify one more time the reliability of the acquisition methodology developed. Secondly, the decision to prepared the different samples with diverse pigments but of the same colour allows to examine the aptitude of the IS instrument to differentiate and characterize colouring agents of similar hues. So, this section will illustrate the potentialities of the IS system to differentiate, characterize, map and monitor simple paint layers during an artificial ageing process. Moreover, the reliability of its response will be verified another time and the suitability of the spectral resolution to distinguish the spectral features will be tested. Finally, a solution to reduce the noise of the obtained reflectance curves will be proposed. As in the precedent section, some difference between the data given by the IS system and by the spectrophotometer are expected but in general the spectra must be in good agreement, especially if it is considered the position and shape of the band that produces the colour.

III.B.3.B Samples

In order to understand if the IS device is able to detect the optical changes during an accelerated ageing process, several samples were prepared. The objective was to deal with systems that were more close to the real cultural objects that the pellets used in the precedent case. The samples were prepared using eight green pigments that are enumerated in Table III.5 with some of its characteristics, including the examination of the prepared paint layers with the optical microscope, OM (see Annex 1 for technical details). The preparation of the samples used in this part of the work was executed as follows: for each pigment that is listed in Table III.5, a relatively small quantity of pure powders (particles) is dispersed in a binding medium, in particular in linseed oil. Then, each mixture prepared in this manner was deposited on a piece of glass in order to obtain paint films. The choice of this class of support was due to its relatively low interaction with the paint layer but also because this material maintains reasonably its integrity when exposed to accelerated ageing processes. The glass employed came from microscope slides that were divided in two parts and the paint layers spread on them have a surface area of approximately 2cm x 3cm. For each pigment, two samples were prepared following this method in order to expose one of the pair to the accelerated ageing process and the other remains unaltered. In this way, after each cycle on the climatic chamber, it is possible to examine any change on the aged sample by comparison with the unaltered paint layers. The first observation is always performed by the naked eye that could detect any modification on the colour as instance but if a reference is available. It can be noticed that all the pigments used to elaborate the laboratory models are of

Table III. 5- Pigments employed to prepare the green paint layer samples and some of its characteristic [38, 73-77, 101, 102, 105-112].

PIGMENT	SAMPLE VIEW WITH OM	CHEMICAL COMPOSITION	PRINCIPAL CHARACTERISTICS	MAIN SPECTRAL FEATURES OF THE REFLECTANCE SPECTRA
Chromium (III) oxide Kremer		Cr_2O_3	Green pigment synthesized since the 19th century. Laurie states that it is used since 1862 even if it could be used before this year	Reflectance maximum ~ 540nm produced by Cr(III) which has a d^3 configuration leading to two strong absorption bands in the visible at approximately at 460 and 600nm. d orbitals splitting in a O_h environment
Viridian Kremer		$Cr_2O_3 \cdot 2H_2O$	Intense bright green-bluish pigment synthesized for the first time by Pannetier and Binet at the year 1838.	Reflectance maximum ~ 510nm -410nm. Higher reflectance than Cr_2O_3. Cr(III) d^3 configuration leading to two strong absorption bands in the visible at approximately at 420-460nm and 580-650nm.
Green Earth Verona Kremer		$K(Mg,Fe^{II})(Fe^{III},Al)$ $[(OH)_2 \mid (AlSi_3,Si_4)\ O_{10}]$	Natural clayey materials used since ancient times. Mainly 2 related clay minerals produce its colour: glauconite and celadonite. Other clay minerals can be present as chlorites and kaolinites	Reflectance maximum ~ 490-540nm d. Typically, the reflectance curves show a slight shoulder on the short wavelength. Colour is produced by several absorption phenomena as the intervalence charge transfer (IVCT) between Fe(II)/Fe(III)
Cobalt green Kremer		Co_2TiO_4	High-performance cobalt titanate with inverse spinel structure. Green blue Co salts developed since the XIX century.	Reflectance maximum ~ 525nm produced by absorption bands of Co(II) in a tetrahedral environment.
Phthalocyanine green Kremer		$C_{32}N_8Br_6Cl_{10}Cu$	Synthetic product. Used after 1936. There are diverse compounds from hues from blue to green yellowish.	Reflectance maximum ~ 500nm. Electronic spectrum dominated by the permitted transition $\pi \rightarrow \pi^*$
Verdigris Synthesized in laboratory		Neutral $(Cu(CH_3COO)_2)\cdot H_2O$ Basic: ≠ mixtures of $(Cu(CH_3COO)_2)$ e $(Cu(OH)_2)$	Synthesized since antiquity. Degradation products of copper obtained under vinegar fumes as instance. Mixtures of ≠compounds with hues from green to blue	Reflectance maximum depends on the verdigris type, medium and on its age in the range ~ 490 - 528nm. Absorption bands: Ligand to metal charge transfer band (LMCT)+Cu(II) in distorted Oh environment
Copper resinate Synthesized in laboratory		Cu(II) salts with abietic acidcon $C_{19}H_{29}COOH$	Synthesized from other Cu greens and mainly during the XV and XVI centuries. Employed in other periods but mostly abandoned since the XVIII century to its tendency to change colour.	Reflectance maximum ~ 535-545nm. Absorption bands: Ligand to metal charge transfer band (LMCT)+Cu(II) in distorted Oh environment
Green Verditer Synthesized in laboratory		$Cu_2CO_3(OH)_2$	Synthetic compound. Same composition as the natural mineral malachite but with ≠ particles shape. 1st recipe written ~ 1657 but maybe used before this year	Reflectance maximum ~ 495-515nm. Absorption bands: Ligand to metal charge transfer band (LMCT)+Cu(II) in distorted Oh environment

green colour. Since one of the aims was to study and test the skills of the developed instrumentation to differentiate and characterise colouring agents, it was decide to use compounds of the same colour, green. So, it will be verified if the IS system can detect the different spectral features of the different compounds and in this basis differentiate the diverse materials, even for those of the same chromatic gamut. The utilisation of green pigments is justified by several reasons. Firstly, these colouring agents have a bell-shaped spectrum that could "push" the IS system to its analytical power limits, due to the presence in general of different types of features to reveal on the reflectance curves of the materials having this hue. Secondly, the maximum of reflectance of green compounds is situated approximately between 480nm and 550nm, where the quantum efficiency of the detector and the emission of the lamps of the IS device are adequate. The selection of the different compounds listed in Table III.5 was justified by their different stability, origin and period of uses. The most part of them are from a commercial source [101] but three of them, the verdigris, copper resinate and green verditer were specially prepared on the laboratory. The details of the synthesis of these compounds is detailed in the Annex 2.

The binding media selected to elaborate the different paint layers was linseed oil. As it has been previously discussed on chapter II, drying oils had been extensively used as binders. In particular linseed oil, has been used by the painters before the XIV century, but has been mostly employed since the XV century. Its wide application is due to the ability of linseed oil to form paint films with good optical and mechanical properties in an adequate time when it is spread in thin layers. Linseed oil is basically composed by oleic acid (14-24%), linoleic acid (14-19%), linolenic acid (48-60%) and by a low percentage (9-13%) of triglycerides from satured fatty acids (palmitic and stearic). Its hardening process has not been completely understood and for this reason it has been studied in different times. It is believed that is an autoxidation process followed by a polymerisation. After a period during which the oil is stable due to the presence of natural antioxidants, the double bounds of the medium are oxidised by atmospheric oxygen giving rise to the formation of peroxidic compounds. Then, a polymerisation process occurs that essentially involves intermolecular coupling of radicals that originate from the decomposition of the products of the precedent oxidation reactions which leads to cross-linked structures. Although a film of linseed oil becomes "touch-dry" in days the cross-linking processes continue for years. There are additives and pre-treatments that can augment the rate of the drying procedure (boiled, blown and stand-oils) [70, 71, 113, 114]. The linseed oil employed was acquired from a commercial source (Lefranc & Bourgeois [115]).

In order to prepare these paint layers samples, it has been used the minimum amount of linseed oil in order to form a dispersion for each pigment in the binding medium that could be easily spread on the glass support forming a thin film. The paint layer has been extended trying to form smooth and homogeneous surfaces avoiding the formation of irregularities that could produce specular reflectance and could interfere with the analysis with the IS device. After its preparation, the samples were let dry for a period of at least 2-3 weeks before being analysed and artificially aged.

The prepared samples are very simple paint layers that could act as models of the real stratum that composed real paintings. As it has been discussed and commented in chapter II, this kind of cultural objects are built in different layers and are much more complex than the samples of green pigments dispersed in linseed oil prepared following the methodology that has been described. However, as a starting point before the study of real artworks it is a useful approach. In addition, these models would be valuable tools in order to reach the special purposes of this section of the research work.

In addition to these samples, a thin film constituted by only linseed oil deposited on a glass support was prepared in order to control separately the effects of the artificial ageing processes on the binding medium. It was treated as the other samples, letting it dry firstly for 2-3 weeks and then exposing it to the artificial ageing process in the same conditions as the green paint layers.

Finally, in order to demonstrate the analytical power of the built IS system to perform chemical mapping another sample was required. The different green paint layers prepared before were monochromatic. In order to verify the potentialities of the developed methodology to measure the visible diffuse reflectance through the IS device to characterize and to map pigments on cultural heritage objects, a polychromatic sample was elaborated. The reason that make this kind of model more suitable for this purpose is that in this manner it is possible to examine not only the quality of the information from the spectral point of view but also from the spatial perspective that is essential for the IS technique. Moreover, when the results will be presented in the following section it will be faced the possibility to reduce the noise of the spectra obtained by worsening the spatial resolution. In these conditions, it has been considered adequate to perform some tests on a sample constituted by a unique support of glass where several areas can be distinguished. These regions are made with the different pigments listed on Table III.5 dispersed in linseed oil. The obtained paint layers where deposited in different areas in a some kind of “rectangular” shaped paint films with different sizes. In some of these portions of the painting model, some of the pigments employed where used both as masstone (which means use the pure pigments) and as a mixture with the white pigment titanium white, TiO_2. The green pigments have in general low reflectance values which had put the IS system to its limits due to the low signal, as it will be commented in the results section. However, during various tests concerning the calibration procedure that will be commented in a next section of this chapter it had been observed too that the system seems to have some problems regarding the measurement of white materials in terms of signal to noise ratio and coherence of the data. For this reason, it has been decided to examine some green pigments, in particular those with the lowest reflectance values that are the phthalocyanine green, the Verona green earth and the verdigris, not only as a masstone but also as a mixture with the TiO_2. In this manner, it will be tested not only the ability of the IS system to perform chemical mapping but also the response of the instrument in this kind of situation that could result problematic for the developed device. The polychromatic sample is supported on a piece of glass of 21cm x 12cm and its distribution in different areas can be observed in Figure III.17 which displays the digital image reconstruction obtained during the analysis with the IS device and the specific pigment or pigments of each zone.

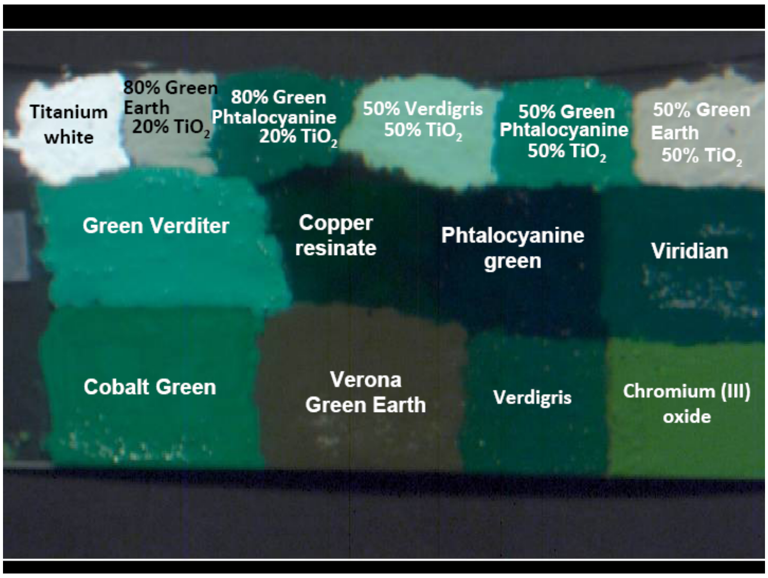


Figure III.17- Digital reconstruction of the image of the polychromatic prepared sample and pigments used on its different areas

III.B.3.C The artificially accelerated ageing process

As it has been previously indicated, the samples were exposed to an accelerated ageing process in order to induce changes on its optical properties and then verify if the IS system allows the detection and monitoring of such alterations of the paint layers. The accelerated ageing process was performed thanks to a light and weathering chamber “Atlas CPS+” (see Annex 1). As it has been discussed in chapter II, the exposition to several agents as the UV and visible radiation, to different pollutants or to changes in temperature can provoke alterations of painting materials as pigments or varnishes.

The experimentation has started with the collection of the diffuse reflectance spectra with the IS device and with a benchtop spectrophotometer, Cary 5 (see Annex 1) of the set constituted by the eight monochromatic paint layers supported on eight different pieces of glass. Each of these mock-ups will be labelled with the name of each pigment. The linseed oil and the polychromatic samples will be treated later separately. This stage was nominated as phase 0. From this moment, the painting models were aged four different times (phase 0, not aged, up to phase 4) and analyzed progressively with the IS device and the spectrophotometer.

The ageing process was planned in order to alternate the exposition to light with periods of darkness up to the time/dose wanted. These rotation was performed in order to emulate in some way the natural ageing process and in particular to provoke the cycles of changes of temperature and humidity that are present in some real conditions as for instance between night and day that can produce alterations as the *craquelure* of the paint layer. Since the equipment employed does not have any instrumentation to control the %RH (relative humidity), a beaker with deionised water was introduce inside the weathering chamber in order to provide local humidity and avoid extremely drying conditions. The main parameters of the ageing program are summarized in Table III.6.

Table III. 6- Parameters of the accelerated ageing process

Phase	Duration (hours)	Irradiance (W/m2)	Chamber Temperature (°C)
light	12	500	~ 46°C
dark	12	0	~ 26°C

Each phase had a total radiant exposure of 108000 KJ/m^2 which corresponds in time for a total duration of the accelerated ageing program of five days. In Figure III.18, there is a picture of the set of green paint layers inside the weathering chamber after being exposed to one of the phases of the ageing process.

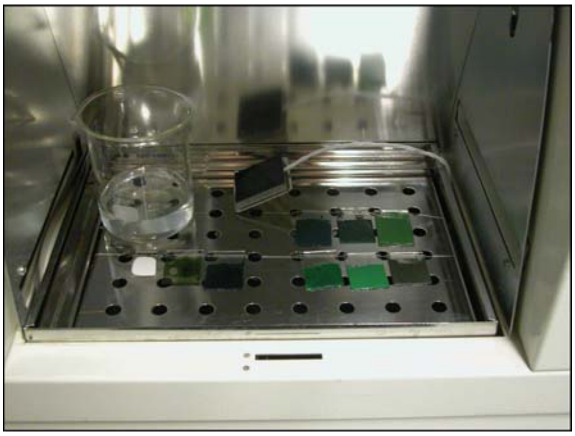


Figure III.18- Set of green paint layers sample inside the light and weathering chamber

For the sample formed by only linseed oil deposited on a glass support has been exposed separately but to the same artificially accelerated ageing program, which means at four different times (from phase 0, not aged up to phase 4) at the same conditions on the light and weathering chamber.

Finally, the polychromatic sample was exposed only to one phase in the same operating parameters summarize in Table III.6 but the duration of the complete program was only 2,5 days that correspond to a radiant exposure 43200 KJ/m^2. In this case, it was considered that only this accelerated ageing exposure was necessary to demonstrate the ability of the system to perform chemical mapping.

III.B.3.D Results and discussion

Different works have been found in bibliography which deal with artificial accelerated ageing processes of materials regarding the field of cultural heritage objects [71, 81, 112, 116-121]. Taking into account these references, it was expected that the alterations that the samples could suffer were basically a general loss of gloss and a possible yellowing due to the hardening and ageing process of the linseed oil medium. These effects should be noted on the reflectance spectra as a diminution of the reflectance and as a displacement of its maximum versus longer wavelength respectively (versus the yellow zone). In fact, these changes on the binding media can be provoked as it has been previously discussed by the electromagnetic radiation, the humidity, the pH environment but also for the presence of the pigments which play many times an important role in this kind of processes. In the particular case of the copper resinate pigment, several works have investigated through different methodologies its change of colour from green to yellow-brown- black [81, 112, 117, 118]. In fact, this tendency to suffer such type of degradation was known by the artists reducing its use in order to prevent the alteration of the paintings [81].

During the accelerated ageing process it could be observed with the naked eye that in general all the samples of the set of eight green paint layers had loss brightness. However, this consequence was evident for the sample made with the pigment viridian, as it can be observed in Figure III.19 where a comparison between a non aged and aged sample is shown. In the case of verdigris and Verona green earth, the loss seemed also important.

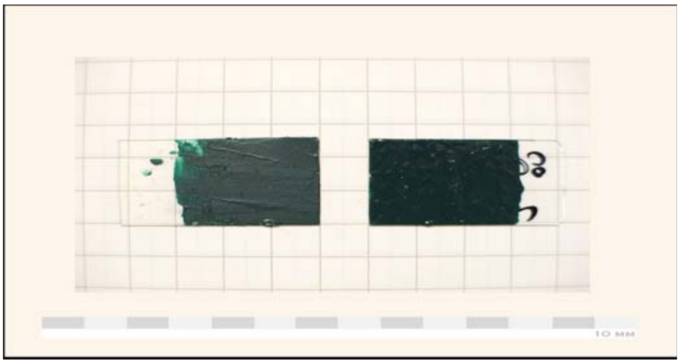


Figure III.19- Viridian samples: exposed to the accelerated ageing process (left) and non exposed (right)

In the case of the copper resinate during the artificial ageing process, it has been observed a change of colour, as it was expected form the references. In particular, in Figure III.20 there is a picture of the copper resinate samples after the phase 2 on the light and weathering chamber that illustrate the yellowing of the aged sample.

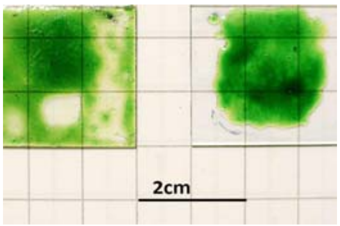


Figure III.20- Copper resinate samples: exposed to the accelerated ageing process (left) and non exposed (right)

Observing the spectra obtained from the set of the eight green samples, it can be noticed that in general the models show very low values of reflectance. This fact is due to the use of the pigments as masstone obtaining green paint layers which shows usually low brightness. The effect of adding a white pigment will be considered when the results of the polychromatic sample will be faced. However, dealing with such low values of reflectance means that it is near to the limit of the sensibility of the IS device. Moreover, in the precedent section it has been already commented the fact that the spectra where coherent but noisy if compared with the results given by the spectrophotometer. The two factors, noisy spectra and low reflectance value (low signal), could produce data difficult to elucidate. So, for this reason it has been decided that in order to improve the instrument it was necessary to increase the signal to noise ratio. Taking into account the precedent technical details that had been previously discussed on this chapter, it can be observed that the spatial resolution is more than enough to study as instance a painting where the details could be generally seen with the naked eye. So, as a solution to improve the quality of the spectra it was decided to reduce the spatial resolution performing a media between various neighbouring pixels of an area. This could be achieved also by doing several measurements of the sample under consideration but this operation could be time consuming so the pixel averaging was choose as a more adequate solution. This operation returns spectra with a significantly better signal to noise ratio, so it has been adopted from this point of the research work. In particular, it is performed a *ad hoc* valuation which compromises the spatial resolution and the quality of the spectra collected. For example, if it is desired to inspect very little details the noise would be higher that if a bigger feature of an artwork is studied. Obviously, it also depends on the distance between the surface analyzed and the instrument or, in the particular case of the horizontal spatial resolution of the step of the rotator. Nevertheless, generally speaking it could be said that the quality of the spectra can be improved if a media of different pixels is performed even if that means a reduction of the spatial resolution but in each particular case, the best compromise is adopted. Finally, it can be noticed as a general observation that the spectra collected with the IS device where in good correspondence with the information furnished by different references and with the information recorded by the integrating sphere spectrophotometer considering the shape and positions of the diffuse reflectance spectra. However, considering the value of the reflectance, the correspondence was not so adequate, that was particularly evident for the pigments with lower values as the green earth. It has been previously discussed that measuring the diffuse reflectance with systems so different in terms of illumination, geometry and of conditions could produce difference on the value of the reflectance. It must not be forgotten that whereas a spectrophotometer is an instrument that operate in a stable and close environment, IS measurements on the contrary are performed in less stable and opened conditions. However in the case of the darker pigments, the differences seem more critical. In fact, it has been hypothesized that is partially due dealing in this range of the signal in which the IS system is put to its limits. As an additional control operations after the phase 3 of the accelerated ageing process the data collected by the developed instrument were compared with the ones furnished by two spectrophotometers (Cary 5 and Cary 5000, see Annex 1).

The changes on the optical properties of the set of green paint samples during an accelerated ageing process could be divided in four groups that will be discussed separately.

- Chromium (III) oxide, Cobalt green and Phthalocyanine green

This group is characterized by being practically unaffected during the ageing process. In fact, those pigments are among the materials widely used nowadays. In Figure III. 21 the spectra of the cobalt green collected with both instrument during the progression of the experiments are represented.

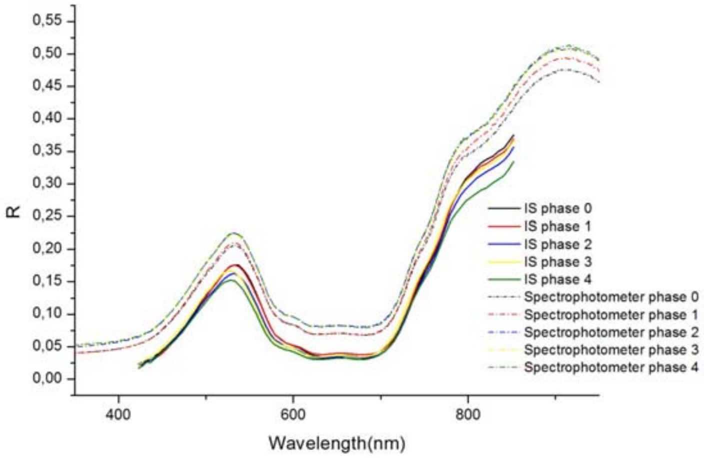


Figure III.21- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the cobalt green sample during the ageing process

It can be observed, that the spectra collected with both instrument are in good correspondence but with different values considering reflectance. However, the general trend of this group of samples can be studied with both instrument. With the progression of the ageing process, the values of the reflectance (especially at the maximum at approximately 525nm) decrease. This is detected as a loss on the brightness of the samples. The spectra obtained with the IS system have a better signal to noise ratio if compared with the results collected on the coloured pellets. This was achieved as it has previously explained by averaging the data of more pixels. The results were very encouraging if compared with the first ones acquired on the mosaic sample fragment M. In fact, it can be noticed that the spectral features in this case are detectable. Co_2TiO_4 is a cobalt titanate with a structure type of inverse spinel where Co(II) occupies both tetrahedral and octahedral sites ($[Co]_t$ $[TiCo]_o$ O_4) and for this reason in the spectra it is possible to observe an absorption band corresponding to an electronic transition concerning the Co(II) Td. It corresponds to the transition $^4A_2 \rightarrow {}^4T_1(P)$ and it could be observed on the spectra in Figure III.21 at 585nm, 628nm and 676nm which is in agreement with the data retrieve in the reference [122]. It should be observed a transition of the Co(II) Oh as a shoulder at ~720nm corresponding to the transition $^4A_{1g} \rightarrow {}^4A_{2g}(F)$ but in the data obtained by IS it can be observed at 756nm. There should be another shoulder at ~535nm ($^4T_{1g} \rightarrow {}^4T_{1g}(P)$) but in the IS spectra it could not be appreciated, maybe because being less intense than the main absorption it has been hidden by it.

- <u>Verona green earth, green verditer, verdigris</u>

This group is characterised by pronounced decrease on the reflectance values during the ageing process, especially if compared with the general values of this optical property. In this case the spectra obtained are quite more noisy, but also because of the low signal level that are revealed. This effect is due probably to two different causes. In the particular case of the Verona green earth sample it has been observed during the preparation of the paint layer that the pigment had an elevate oil absorption. Each colouring agent requires a different quantity of binder. The relatively high proportion on linseed oil together with its quite low reflectance value has produced the pronounced and relatively elevated decrease of this optical property during the progression of the accelerated ageing process.

On the cases of the green verditer and verdigris the cause could be another one. Both are copper based pigments. There are several works in literature that have studied the effect of copper in the oxidation of drying oils [117, 123]. Copper salts have being demonstrated to have a great influence on the ageing processes regarding oil films increasing their rate of degradation. These alteration processes could lead to changes in the colour (yellowing-browning). It seems that copper ions take part on such oxidation processes and that copper resinate and verdigris pigments show a higher reactivity. In fact, the copper resinate sample that will be treated separately has turned its hue from brilliant green to a dirt-yellowish green. This can produce the major decrease detected on the reflectance value of verdigris and green verditer samples. However, it must be considered that also in this case it could be some influence of the same effects described for the green earth sample, because these pigments show low reflectance values and could have a relatively high proportion of linseed oil.

In Figure III.22 the spectra acquired by the IS device and the spectrophotometer during the progression of the accelerated ageing process of the green earth sample is displayed.

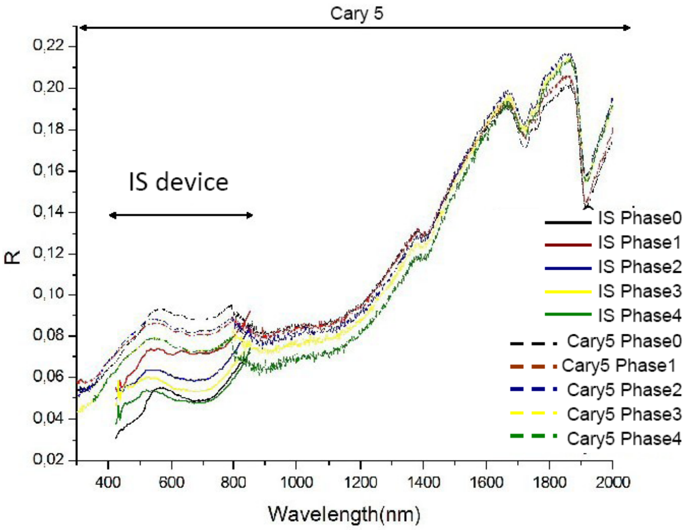


Figure III.22- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the green earth sample during the ageing process

From the phase 0 up to phase 4 the reflectance values decrease. The IS spectra are in good agreement with the spectrophotometer data. However, the reflectance curve collected with the IS device in the phase 0 shows some kind of distorted shape and intensity values lowest than the expected. It is thought that this is due of some kind of instrumental error during the acquisition of only this sample because this kind of problem has not been detected in the other cases. Nevertheless, the IS device collected spectra are in good agreement with the spectrophotometer and where the spectral features of the material could be observed. There is a strong charge transfer absorption in the near-UV and several d-d ligand field and intervalence charge transfer transitions superimposed to the latter. This lead to the obtained reflectance spectra with a slight shoulder on the short wavelength and a slightly higher reflectance values in the red region [105].

- Viridian

This sample shows a strange behaviour because there is a maximum in reflectance in the UV which increase substantially its intensity from the non aged sample to the altered sample. In fact in Figure III.19 it could be observe that the changes are detectable with the naked eye than the sample seems more bluish after the accelerated ageing process. The spectra collected with the IS device and with the spectrophotometer during the alteration progression are compared in Figure III.23.

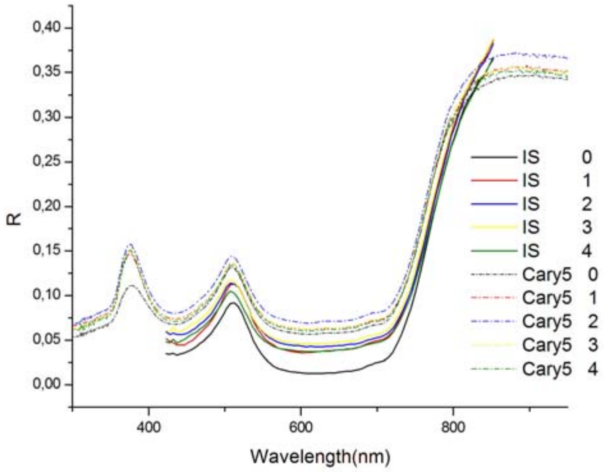


Figure III.23- Reflectance Spectra obtained by the IS device and by the spectrophotometer of the viridian sample during the ageing process

Unfortunately, the strong change in the reflectance peak is before 400nm and in this region the IS device does not work. However, it is an interesting effect that is completely different than the alterations suffer by the other samples. As in the other cases the information of both system is in good correspondence despite the difference on the intensity of the reflectance and the IS device is able to identify the characteristic absorption bands of this sample that are due to the Cr(III) having a d^3 configuration.

- Copper resinate

The sample that had experienced the most dramatic changes during the progression of the accelerated ageing process has been the copper resinate paint layer. In this case the brilliant green colour has turned yellowish and as in the many other cases the reflectance has decreased. In Figure III.24 the spectra obtained with the IS device is showed during the accelerated ageing process from the non aged sample (phase 0) until the last ageing step (phase 4).

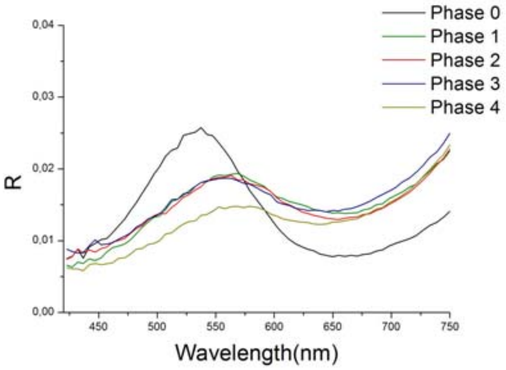


Figure III.24- Reflectance Spectra obtained by the IS device of the copper resinate sample during the ageing process

As in the other cases the decrease in reflectance is traduced on a loss of glossy whereas the yellowing process is detectable as a displacement on the reflectance maximum to higher wavelengths. The spectra are in good agreement with the ones obtained by the spectrophotometer that are not illustrated because due to the really low reflectance value that has produced noisy spectra with the commercially available instrument and if the data were displayed together it could lead to confusion. As it has been discussed before, the copper resinate could alter the binding media increasing its rate of degradation. In fact some authors retains that the yellowing is due to these processes [123]. However, more recent studies state that the copper chemical environment, especially in a lipid binder, can undergo local rearrangements which could lead to changes in the colour. It seems that copper complexes are primarily involved in pigment embrownment. The changes on the Cu coordination could lead to these changes of colour. In fact the spectra illustrated on Figure III.24 have its origin on the structure of the Cu(II) in this pigment. In the near UV range, there is a strong absorption carboxylate to copper charge transfer partially cover by the absorption of the terpenic resin. In the red region, the broad band at ~700nm is characteristic of square-pyramidal Cu(II) complexes. In this structure (as in the verdigris) four carboxylic coplanar oxygen atoms coordinate the Cu(II) and in the two apex positions are occupied by a water molecule and a neighbouring Cu(II). The symmetry centre in this structure is halfway between the metal ions producing an asymmetric ligand charge distribution for each Cu (II). This situation allows the d-d transitions producing intense colours (Laporte selection rule) [77, 81, 112, 116, 117].

In order to verify the effect that the accelerated ageing process has on the binder medium without the pigments, the prepared sample has been studied only with the spectrophotometer equipped with an integrating sphere Cary 5 in the range from 350nm to 900nm. In Figure III.25 a detail of the spectra collected is illustrated.

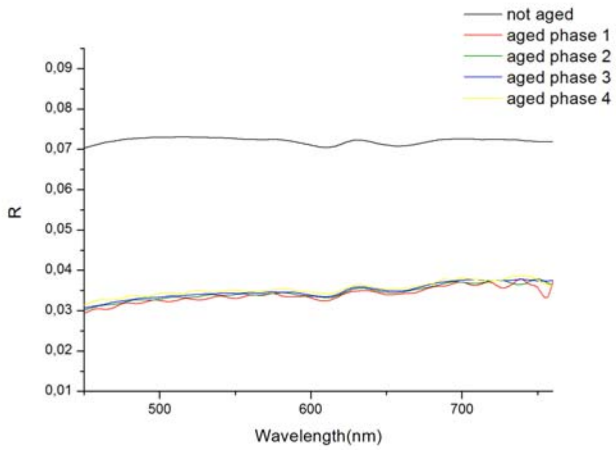
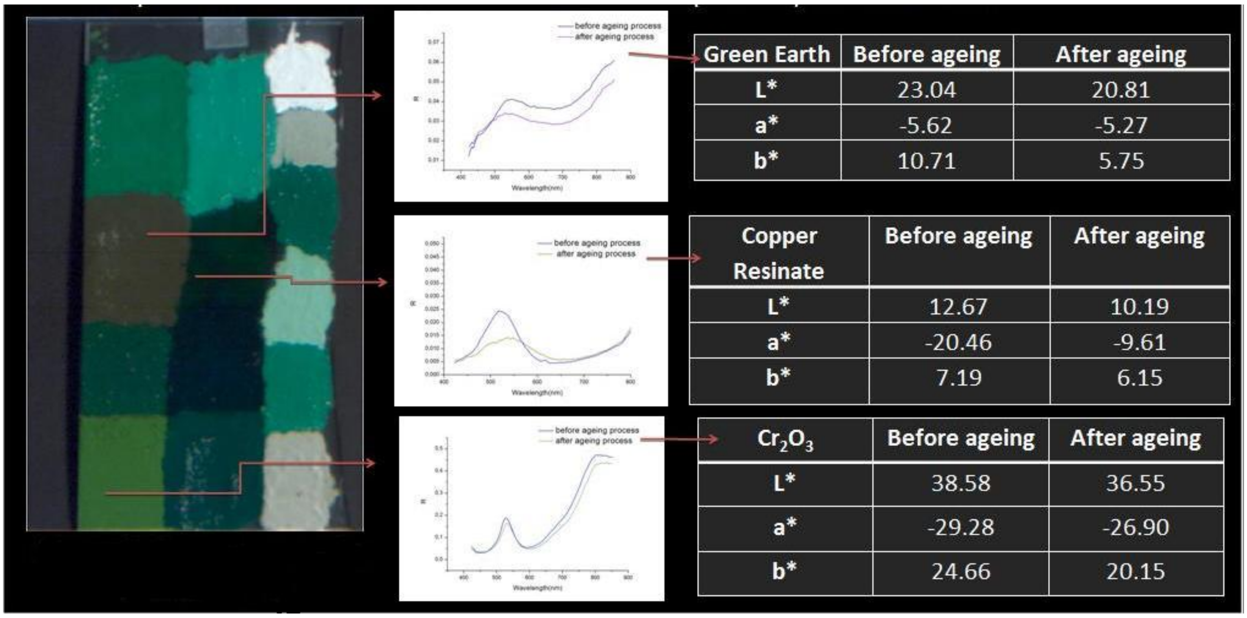


Figure III.25- Reflectance Spectra in the range from 450nm to 750nm obtained by the spectrophotometer on the linseed oil sample during the ageing process

The spectra of the linseed oil in general display a low reflectance value with an absorption towards the UV. In the detailed zone represented in Figure III.25 it can be observed that between the phase 0, non aged sample, and the following step of the ageing process the reflectance value decrease as it has been observed for the green samples previously discussed. It can be observed two small bands at 600nm and 650nm but they do not seem to change substantially during the progression of the experiments. Moreover, they are so slight that they have not been observed in the green samples. In literature, it has been reported that due to ageing processes the films formed by linseed oil tend to turn yellow. [71, 114, 116, 118-121, 123]. However, this effect has not been observed on the studied sample during the progression of this experiment. It could be possible that the ageing still is in its early stages and to detect evident signs of degradation a higher radiant exposure is required or the coincidence with other factors as temperature or chemical processes that can accelerate the alteration mechanisms, as the previously cited Copper. In fact, in the spectra collected it was not observed the absorption which is responsible of the yellowing of this binder. It is a strong and broad band which extends from the UV and that is originated from the conjugated systems which are products of the degradation process of the linseed oil.

The polychromatic sample was analysed by means of the IS device. Even if this sample has only been exposed to the artificial ageing process until a radiant exposure of 43200 KJ/m^2, the effects on the pigments have been the same observed on the monochromatic paint layers. In Figure III.26 some of these results are displayed.



Green Earth	Before ageing	After ageing
L*	23.04	20.81
a*	-5.62	-5.27
b*	10.71	5.75

Copper Resinate	Before ageing	After ageing
L*	12.67	10.19
a*	-20.46	-9.61
b*	7.19	6.15

Cr_2O_3	Before ageing	After ageing
L*	38.58	36.55
a*	-29.28	-26.90
b*	24.66	20.15

Figure III.26- Mapping of the polychromatic sample performed by the IS device showing the reflectance spectra of Cr_2O_3, copper resinate and green earth areas and its chromatic coordinates before and after the ageing program

It is possible to observe in Figure III.26 a methodology to solve different analytical problems regarding cultural heritage objects using the IS device. The digital reconstruction obtained allows, thanks to data processing using matlab routines, to select the particular area to study and its size in order to get a compromise between spectral quality and spatial resolution. In these regions of interests it is possible to obtain the diffuse reflectance spectra and the chromatic coordinates.

In this sample, there are some areas where several pigments where mixed with TiO_2 in order to study the effect of this white pigment. As it will be discussed in the following section, occasionally some problems have been encountered when dealing with white materials. Figure III.27 represents the reflectance spectra of different region of interests where green earth and phthalocyanine green pigments are used. In the latter case in the left part of Figure III.27, it can be observed that the addition of TiO_2 seems to produce only an increase on the reflectance as it is generally expected. In all the cases it is possible to observe the permitted transitions $\pi \rightarrow \pi^*$ which are responsible of the colour of this pigment [124]. On the case of green earth, illustrated in the right part of Figure III.27, the areas where the pigment has been used in conjunction with the TiO_2 present a slightly more noisy spectra. However, the effect does not seem critical. The effects of the ageing are basically the same, a decrease in the reflectance values.

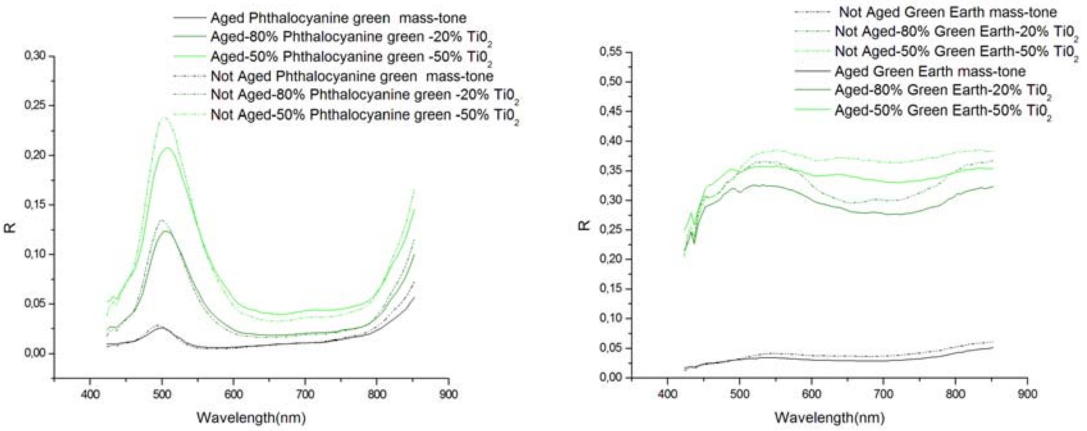


Figure III.27- Reflectance Spectra obtained by the IS device of the areas containing green earth (right) and phthalocyanine green (left) pigments before and after the ageing process

Finally, as it has been mentioned before during the phase 3 of the ageing process of the set of monochromatic samples, diffuse spectra were collected by means of three systems: the IS device, a Cary 5 and a Cary 5000 spectrophotometers. In Figure III.28 the spectra collected with the three instruments for the sample of phthalocyanine green are displayed.

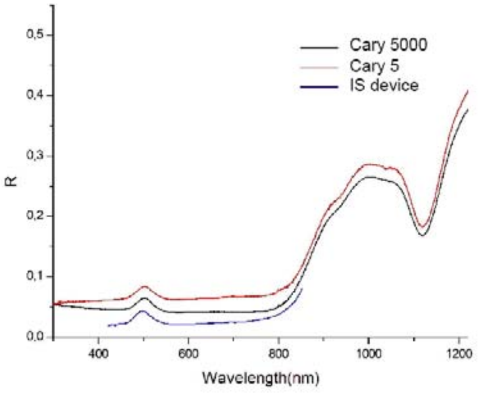


Figure III.28- Reflectance Spectra obtained by the IS device, the Cary 5 and Cary 5000 spectrophotometer after the third phase of accelerated ageing process on the sample of phthalocyanine green pigment.

As it can be observed in the graphic, both spectrophotometer show differences on the reflectance values comparable to the differences retrieve respect the IS device. Using such different conditions it is possible to find diverse values in the intensity but in this case the fact to use samples with considerably low reflectance can influence too on the results collected. The spectra obtained display the same features and the same proportion between bands which is essential in order to obtain information about the composition of materials. The difference between instruments are tolerable as it can be observed in Figure III.28 and for this reason and the results presented in this part of the work it can be considered that the IS device may be a valuable analytical tool to obtain diffuse reflectance spectra.

III.B.3.E Conclusions

The experiments performed employing samples of green pigments dispersed in linseed oil that had been exposed to accelerated ageing process had demonstrated that the IS system is able to characterize, map and monitor paint layers. The multiple purposes of this section of the work had been reached. During the experiments it has been possible through the IS system to monitor the changes provoked by the artificial ageing on the samples. The validity of the data was verified thanks to the comparison with the results furnished by an spectrophotometer. It can be concluded that the developed IS methodology to acquired diffuse reflectance spectra is consistent. The spectral features of the paint layers had been individuated whichs allow to characterize the pigment. The quality of the reflectance curves collected had been improved performing an average on neighbouring pixels of the detector. This operation unfortunately implies a loss on the spatial resolution but the compromise between the two factors consents to obtain spectra which display well defined band and the Matlab routines allow to easily define these parameters permitting to be versatile and accurate depending on the requirements of the different analytical problems. Despite the decrease on the spatial resolution, the system is capable to perform chemical mapping differentiating the different regions of interest on polychromatic surfaces as paintings. As a general conclusion, it could be said that these experiments had demonstrated the potentialities of this kind of system to characterize, map and monitor materials regarding the cultural heritage field in a non destructive way and its possible roles in a multi-technical approach. The technique suffers the limits of diffuse reflectance information in the visible range as an analytical tool (i. e. low fingerprinting ability). However, the data collected during these experiments show that a IS systems like the one developed could have many applications on the field of chemistry of cultural heritage, especially if the interpretation of the reflectance curves is employed in combination with other techniques as XRF. If these data are compared with the ones obtained during the first tests it is obvious that the changes performed have notably improved its analytical skills. In addition, it has permitted to the research teamwork to get experience from the technical point of view and also on the elucidation of the information.

III.B.4 CALIBRATION PROCEDURE

III.B.4.A Calibration procedure to obtain Reflectance data

The developed IS system collects through the CCD detector signal intensity counts not reflectance values. In order to correct or transform raw signal data into reflectance or absorbance units, it is necessary to acquire a reference white signal under the same illumination conditions of the sample. In this particular case, this is achieved by superimposing on the objects surface a white screen of known spectra in the wavelength range of interest.

The diffuse reflectance of the object under consideration for any pixel $R_{n,m}$ within the sensor is calculated by the following formula:

$$R_{n,m} = \eta \frac{(S_{n,m} - s_{n,m})}{(W_{n,m} - w_{n,m})}$$

where m = 1; …; M (M = 1024) spans the spatial dimension and n = 1; … ;N (N = 1344) spans the spectral dimension. $S_{n,m}$ is the colour signal (the raw signal collected by the sensor), $W_{n,m}$ is the reference white signal and η is the reference white spectral reflectance. On the other hand, $s_{n,m}$ and $w_{n,m}$ represent the signal-dependent offsets for the colour signal and the reference white, respectively. They are calculated as the mean of the first four bands of the acquired signal, where no useful signal is present due to both the low sensitivity of our CCD and the low emissivity of the lamps. Formalizing, it could be written:

$$x_m = \sum_{N=1}^{4} X_{n,m}$$

where $X \in \{S, W\}$ and $x \in \{s, w\}$. The choice of signal-dependent offsets, or dark signals, allows to compensate for possible non-linearities of the camera, which cause the dark current signal to be dependent on the useful signal. As it is well known in the astronomical image processing community [125], dark current values are always signal and pixel dependent. The most correct procedure would be that of subtracting to each pixel the corresponding dark current value, acquired at the same temperature conditions as the active frame. As this would require doubling the number of acquisitions for each frame, a good compromise [125] is that of using inactive pixels to compute a mean value for the dark current. Averaging the offset along several samples allows to isolate the contribution of the dark current from that of the dark current random noise term.

The reference white used to calibrated the IS system is based on a white paper card standardized to a 99% (R= 0.99) Spectralon [126] diffuse reflectance tile with known properties in a wavelength range where the IS system works. This procedure is justified because the instrument was built to study large sized samples, as mural paintings. The 99% reference white at disposition covers an area on the range of not many cm^2 which is insufficient to be applied to most of the interesting applications. Indeed, one of its principal assets is its capacity to study large surface regarding cultural heritage objects. Moreover, this kind of standards are expensive, delicate and had been mostly developed for calibration procedure regarding spectrophotometers where the measurement conditions are totally different.

Accurate results require the best calibration procedure, otherwise erroneous conclusions can be inferred. Calibration in Imaging spectroscopy is subject to all the error contributions of conventional spectroscopy (noise, drift, non-linear response of detectors, wavelength-dependent errors) as well as the two-dimensional or spatial error components associated with camera devices and illumination (readout errors, inconsistent detector responses, quantization errors, and non-uniform lighting). This procedure must also consider effects as physical or chemical changes in samples such as texture or particle size, instrument changes due to any kind of instability, ageing parts of the instrumentation or environment conditions (temperature, humidity ..) [127]. For all these reasons it has been decided that in order to improve the methodology to measure VIS diffuse reflectance spectra through the IS system, some tests and investigations should be performed regarding the calibration procedure.

This section will be faced divided in two parts. The first ones regarding reference materials and the second one to calibration correction and procedure that could be performed in a system like the developed IS device.

III.B.4.B Standards for diffuse reflectance measurement

The white paper card standardized to a 99% Spectralon tile is a satisfactory reference for the diffuse reflectance measurement through the IS system. However, in order to reach more robust results it was decided to investigate possible alternatives that could represent an improvement on the methodology. The aim of this section of the research work was to individuate a better reference material for the calibration procedure that could be obtained in relatively wider surface at a reasonable cost because one of the purposes of the IS approach was to be affordable.

One of the fundamental factors in producing accurate measurement of reflected radiation is the need for stable and easily used standards. Many different materials had been used for this purpose: chalk, magnesium oxide, ceramic tiles, barium sulphate or PTFE. Both the CIE and ASTM have agreed that the ideal standard to measure reflectance diffuse spectra is the perfect reflecting diffuser. This is an ideal material which exhibits no absorbance over its range of use that reflects all radiation in a cosine response to the incident angle of the illuminating beam. While such material exists, many attempts have been made over the years to individuate a material that is close to that ideal concept. W. Erb of the Physikalisch-Techniche Bundesanstalt (PTB) has characterized an ideal standard as having the following properties [128]:

i. it is transportable, or if not transportable, then easily reproduced with high reliability
ii. stable with respect to time, radiation temperature, atmosphere, etc..
iii. homogeneous, with a smooth surface
iv. diffusely reflecting
v. spectrally non-selective
vi. non-transparent (not translucent)
vii. non-fluorescent
viii. easy to handle.

Two materials that are widely used to fulfil this concepts are Barium Sulphate and PTFE. Spectralon is a sintered PTFE material which exhibits almost perfectly Lambertian reflectance over the 200-2500nm range that is perhaps the most commonly used standard for such purposes. Both PTFE and barium sulphate suffer from drawbacks and can change its reflectance properties in time due to ageing or interactions with pollutants [128].

After several bibliographical research, it has been decided to try to prepare a standard for diffuse reflectance measurements based on barium sulphate. This standard has some drawbacks as overtones due to water absorption on the NIR or its fragility. However, it presents several characteristics which are convenient for the particular purposes regarding the developed methodology with the IS system. It is a low cost chemical compound which can be prepared in form of paints to cover wide surfaces and its problem in the NIR or UV region are out of the wavelength of interest.

Several paint recipes were found in literature which could be useful [129-131]. Several procedures where experimented upon these references and different tests on the laboratory including the compression of pure barium sulphate powder following the same method that in section III.B.2 or to bond it to an adhesive support. All these operations did not succeed due to the low mechanical properties of this material. At this point the research was directed to the elaboration of barium sulphate water based paints with PVA (polyvinylalcohol) as a binder. After different tries on the laboratory in order to individuate the adequate proportion, methodology and support to deposited the $BaSO_4$ paint film an optimal procedure was found. It consists on diluted an adequate quantity of PVA in the minimum amount of water at 70°-80°C. When a solution is obtained, the powder of pure $BaSO_4$ is added. Then, the solution is stirred and heated without boiling until the fluidity is adequate to being spread on a glass support (scratched or not). In order to obtain an adequate surface it is essential to deposited the paint film only by pouring avoiding air bubbles and other defects. The adequate proportion of PVA/ $BaSO_4$ is 1% (w/w). To evaluate the quality of the samples reflectance measurements with an spectrophotometer and other aspects as usefulness and resistance were considered. In figure III.29 some of the numerous samples prepared are illustrated. It can be observed that the white paint prepared was deposited on different supports.

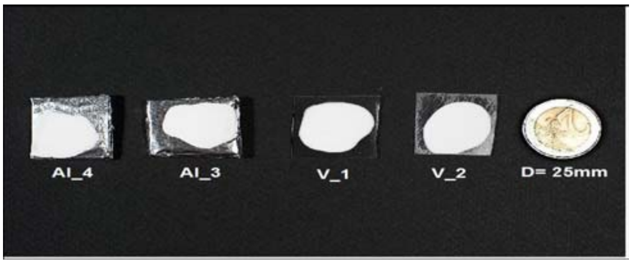


Figure III.29- Various 1% PVA/ $BaSO_4$ paint films prepared

In order to understand if this white reference paint shows better properties as standard from the paper card, diffuse reflectance measurements were performed on the spectrophotometer Cary 5. In Figure III.30 it is illustrated a comparison of the spectra obtained of the 1% PVA/ $BaSO_4$ paint film on glass support and the card paper used as reference. It can be observed that the prepared white film displays better performances as a white standard than the paper usually employed in the wavelength of work range of the instrument.

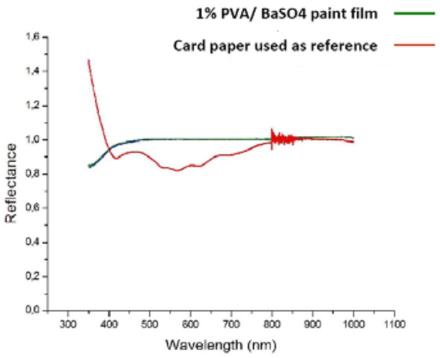


Figure III.30- Comparison of the diffuse reflectance spectra of the 1% PVA/ $BaSO_4$ sample and of the white card paper standardized to a 99% Spectralon tile

The next step was to prepare a greater surface in order to be applied to the study of wider surfaces. A white reference was elaborated with the 1% PVA/ $BaSO_4$ paint film on a glass support of 50cm x 70cm. Several tests were performed measuring the samples prepared to solve calibration problems with the IS developed system. The obtained spectra were disappointing in some cases. The reflectance curve was more noisy than in other cases and with some "spike" in particular in the short wavelength interval. In Figure III.31 the IS diffuse reflectance spectra is showed.

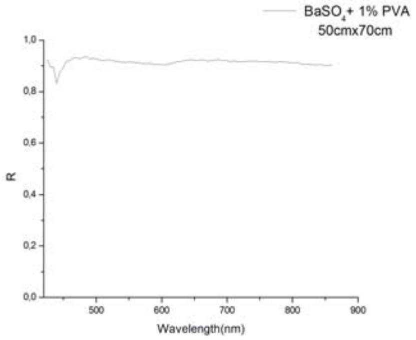


Figure III.31- Diffuse reflectance spectrum of the 50cm x 70cm 1% PVA/ $BaSO_4$ sample

These effects are probably due to the high scattering properties of the barium sulphate together with the illumination system and to the response of the detector when it is close to the saturation.

Despite these results, it has been decided to perform an analysis with this reference on a real sample in order to compare the results obtained by the IS device with both calibration materials. It has been performed on a mural painting study that will be discussed on the next chapter. However in Figure III.32 the diffuse reflectance spectra of a yellow region of the artwork obtained with both references are illustrated.

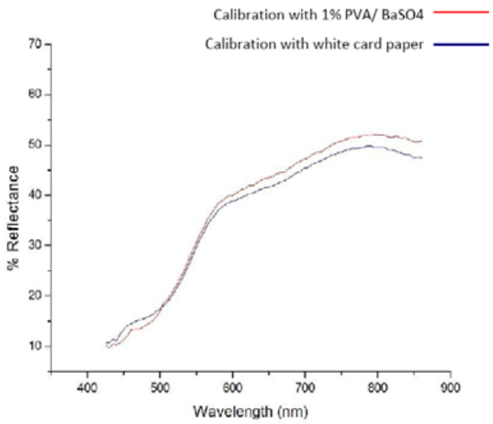


Figure III.32- Diffuse reflectance spectra of yellow part of a mural painting obtained employing the different calibration white references

As it can be observed on the Figure III.32, the employment in the calibration procedure of the developed 1% PVA/ $BaSO_4$ paint film if compared with the white paper card standardized to a 99% Spectralon tile does not lead to a particular improvement of the data obtained. For this reason, it had been concluded that the reference based on paper is convenient and in order to improve the calibration method other solutions must be search.

III.B.4.C Possible calibration solutions

The calibration transformation employed in the procedure described in the section III.B.4.A is often termed a one-point calibration since the transformation is based on a single reference standard. Mathematically, however, this is a two-point linear approximation model with measured endpoint values at 0 and 100% reflectance. This simple procedure requires only two calibration spectra: one of the total reflectance standard and of the dark current [127].

Better results could be obtained when more than two standards can be measured which span the reflectance or absorbance space of the expected samples. When true calibration spectra are available for a collection of standards, an alternative modelling approach could be available by fitting least squares regression models to the true versus measured values for the set of all standards. It could be employed different models a first order linear model with coefficients or a second-order quadratic model [127]. This solution is not adequate taking into account the characteristics of the IS system developed because it will required more references andcould be problematic.

One of the advantages of the IS system is the possibility to measure large sized surface. It could be possible to add internal standard materials, which would fill a little part of the field of view. If they are calibrated and have known spectra, then correction models may be computed to realign the measured data. Corrections in both wavelength or peak position and reflectance or absorbance intensities can be determined. The operation can be performed by using a single point or a multiple-point linear regression-based adjustment. Unfortunately, this depends on the internal standards available. These internal standard-based corrections are global corrections applied to the entire image [127].

Internal standardisation could represent a solution in the particular case under examination. Unfortunately, this calibration procedure was not tested for an unexpected unavailability of the references that were intended to use (Spectralon 99% and Labsphere grey tile of 2% diffuse reflectance) but this procedure could represent an improvement on the methodology that will be interesting to test.

III.B.4.D Conclusions

The calibration procedure in order to obtain from the raw data diffuse reflectance values has been discussed. A white paper card standardized to a 99% Spectralon tile is the reference for the diffuse reflectance measurement through the IS system which leads to adequate results. Nevertheless, it has been investigated the possibility to obtain more consistent data through the improvement of this essential procedure of any analytical method.

The possibility to use another white reference materials has been considered, including several tests with a barium sulphate paint that could be employed as a standard. During these experiments, it had been observed in some occasions that the IS device furnished more noisy spectra if compared with the information obtained in the precedent section regarding the ageing process on green paint samples. This seems to be provoked when analysing high scattering materials that could highly diffuse the light coming from the sources and resulting in a saturation of the detector. However, this fact is not generally critical for the analysis that are of interest in the chemical for cultural heritage field. After a trial measurement on a mural painting using the barium sulphate and the white card paper as references, it has been concluded that the employ of the prepared samples does not imply an considerable improvement and for this reason the material utilized to calibrate the IS system is the white paper card standardized to a 99% Spectralon tile.

Finally, some possible improvements on the calibration procedure has been discussed as the use of internal standards during each measurement. Unfortunately, this possibility was only contemplated from a theoretical point of view due to the impossibility to perform the test during the research work.

III.B.5 IMPROVED MEASUREMENT SETUP AND PROCEDURE

The different measurements performed in this section had involved different modifications and improvements that had implicate a significant progress in the quality of the information obtained. As it can be noticed, the development of this procedure to acquire visible diffuse reflectance spectra with the IS device has occupied a great part of the research work but as it is has been said before, the results are worthy of these efforts. Thanks to the precedent tests it has been identified the spectral wavelength range were the system is reliable, an adequate spectral resolution to distinguish the spectral features, a solution in order to obtain reflectance spectra with a satisfactory signal to noise ratio in spite of the spatial resolution and an adequate calibration procedure. It has been observed during these measurements that this analytical procedure through IS system has potentialities for the characterization, mapping and monitoring of paint systems. In this section the principal technical characteristics and the basis of the methodology of analysis will be summarize in order to get a general perspective and a certain knowledge of the "practical" procedures and kind of information/interface reached. In Table III.7 the main characteristics of the IS system are summarize.

Table III. 7- Principal characteristics of the IS device

Spectrograph	**Specim ImSpector V10**
Sensor	Hamamatsu C8484-05G CCD
Wavelength range	420nm -850nm
Spectral resolution	Average ~5.2nm
Illumination system	• 70W metallic iodide/100W Incandescence lamps (small objects, laboratory measurements) • 250W metallic iodide/500W halogen lamps (*in situ* measurements of large sized objects)
Geometry	0°/45° or 45°/0°/45° depending on the size of surface analyzed
Objective	Canon f=25mm and Computar f=16 mm
Rotation Stage	Physik Instrumente M-062

From the practical point of view, the acquisition setup adopted when a laboratory measurement is performed is represented on Figure III.33. If it is required, another pair of lamps could be added in order to procure an homogeneous illumination. *In situ* analyses are performed following the same methodology but generally it requires a more powerful illumination system (250W metallic iodide/500W halogen lamps). However, this depends of the kind of artwork that must be studied and previous to the acquisition these factors are valuated in order to identify the most adequate setup for each particular case.

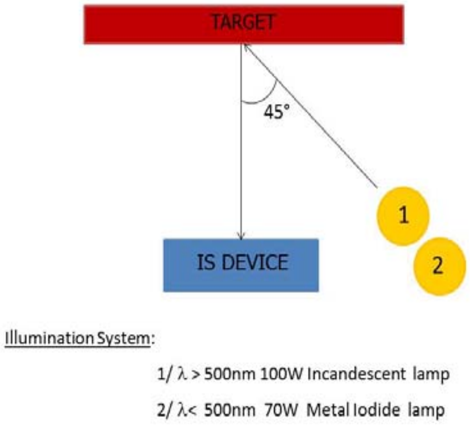


Figure III.33- Acquisition setup adopted with the IS device

From the practical point of view, after the identification of the adequate device-sample distance, horizontal field of view and the focus operation, the optimal exposure times with the employed lamps are decided. It must be controlled that the signal is good enough but at the same time the detector should not saturate. Obviously, all the precautions are taken in order to avoid any alteration on the object under consideration that in the case of chemistry for cultural heritage is a critical issue. Then, the acquisitions is performed in four steps: white reference with metallic iodide lamp(s), white reference with halogen/incandescence lamp(s) and then two measures for both kind of emission source for the sample surface. The procedure could seem quite long but it is not considering the large amount of data collected. Moreover, when studying objects *in situ*, the first operations are the longer ones because the environment could present practical problems as the lack of space but when the setup is ready the analyses are relatively short.

After the acquisition of all the information required (sample and white reference), the processing through Matlab routines (specially developed by the LUXOR and DEI laboratories) allows to digitally reconstruct an RGB image of the surface examined. However, it is not a simple "picture" of the sample because using the software create to handle them it is possible to select regions of interest and obtain the diffuse reflectance spectra and the chromatic coordinates. The size of the areas/point studied can be easily decided by the matlab routines. In Figure III.34 an example of the information acquired is represented.

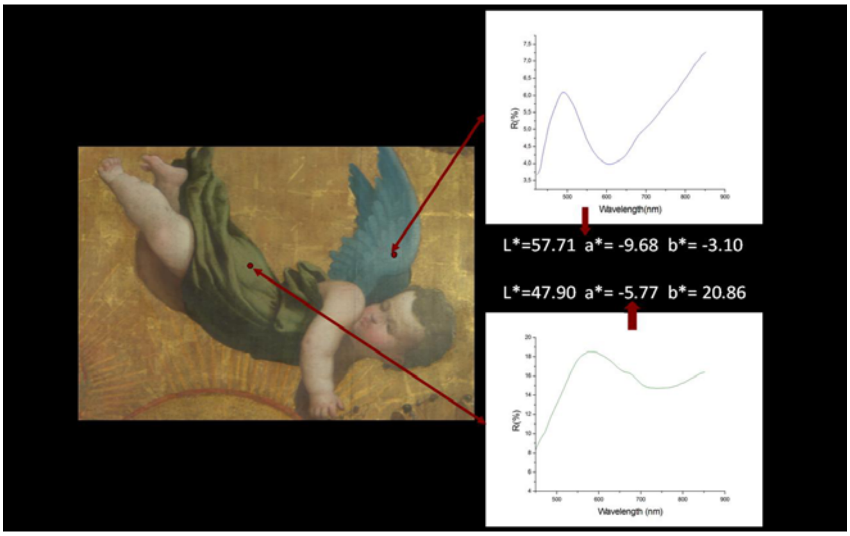


Figure III.34- Example of the obtained information through the developed methodology

It can be observed that the amount of data collected is really large because the image reconstruction contains diffuse reflectance spectra on the 420-850nm range for each point/pixel.

Even after averaging of various neighbouring pixels to improve the quality of the spectra the information is really vast and could have different application. Apart the potentialities to characterize, map and monitor different materials and learn about the chemical composition of this sample which is a really important task, the acquired data can be used too for archive purposes or for virtual restoration operations that could be really useful to investigate the aspect after different operations. On the other hand, the scheme showed in Figure III.34 represents a possible starting point to a more efficient data management when dealing with a concrete work of art. The information collected though diagnosis, archival and art-historical research, restoration process, conservation conditions…. tends to be not totally exploited in many cases resulting in a not efficient management. If the information is collected and then it is organized in a handy flow chart, it would be a powerful tool for the scientific, restorers, curators,… that had to collaborate in such kind of study. Indeed, the prospective for IS device is to be a key role instrument in a multi-technical mobile approach (that would be introduced in the next chapters) where it could represent a powerful tool in diagnosis, mapping and monitoring but also could furnish the handy interface to administer the data and store all the information in a digital and efficient management. This procedure together with multivariate analysis that could be applied to the hyperspectral cube in order to re-elaborate the data and obtain a more evident or handy sets, are two future areas of development for the IS device.

III.C Development of a measurement methodology in transmittance mode in the visible range with the IS device

The possibility to study some samples as stained glass windows in transmittance mode represents an interesting challenge in order to study the chromophores of vitreous materials. This kind of samples are usually relatively large objects that could be formed by numerous glass *tesserae* and the IS system could be a valuable analytical tool in such kind of studies. For this reason it has been decided to dedicate part of the research to set up a measurement modality to acquire visible spectra in transmittance though the built instrumentation. The previous section has deal with the methodology to acquire diffuse reflectance spectra in the 420-850nm interval. This part of the work is still useful because some aspects that have being considered previously are in common when working in transmittance mode. The issues considered about the illumination system, wavelength range, spectral resolution and improvement on the signal to noise ratio are valid when studying transparent samples with this methodology. However, to achieve an acquisition procedure in transmittance mode further tests are required.

III.C.1 ACQUISITION SETUP IN TRANSMITTANCE MODE

The acquisition setup that had been experimented is illustrated in Figure III.35. As it can be observed on the scheme, it is conceptually very similar to the method of collecting diffuse reflectance spectra. The diffuser is required in order to furnish an homogeneous illumination and to do not saturate the CCD detector. It must be placed between the sample and the illumination system.

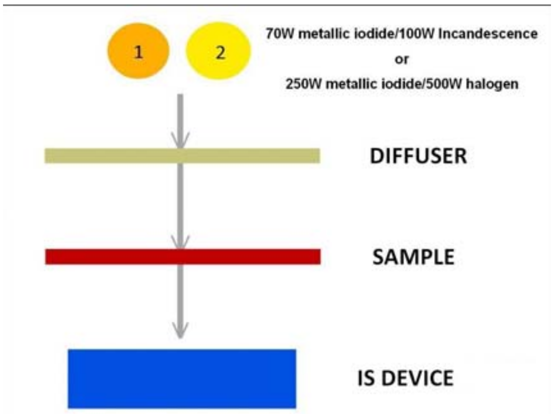


Figure III.35- Acquisition setup in transmittance mode with the IS device

In this case the signal recorded by the detector is the intensity of light that is transmitted through the sample, thus the light that is not absorbed by the vitreous medium. Transmittance is the fraction of incident light that passes through a sample. To transform the raw data collected into transmittance it is necessary to perform another measurement in the same conditions but without the sample, which means on the scheme of Figure III.35 to remove the red layer, measuring the intensity of the incident light that arrives from the emission source through the diffuser. So transmittance of the object under consideration for any pixel $T_{n,m}$ within the sensor is calculated by the following formula:

$$T_{n,m} = \frac{I_{t\,(n,m)} - i_{t(n,m)}}{I_{0\,(n,m)} - i_{o(n,m)}}$$

where m = 1; …; M (M = 1024) spans the spatial dimension and n = 1; … ;N (N = 1344) spans the spectral dimension. $I_{t\,(n,m)}$ corresponds to the intensity of the light transmitted through the sample that arrives to the detector and $I_{0\,(n,m)}$ is the intensity of the incident light. On the other hand, $i_{t(n,m)}$

and $i_{o(n,m)}$ represent the dark current for the I_t and the I_o, respectively and they are calculated as for the reflectance case as the mean of the first four bands of the acquired signal. As for the diffuse reflectance measurement, the spectra have been obtained by juxtaposing at 500nm the signal intensity measured with the metallic iodide lamp in the blue region and that obtained with the halogen lamp in the long wavelength interval. In order to collect the data of a sample four measurements are required. Firstly the incident intensity of light with metallic iodide lamp(s) and with incandescence/halogen lamp(s), and then two measures to obtain the fraction of incident light that passes through the sample with both emission source. The selection of the illumination system to use (type, number and power of lamps) depends on the size of the surface that is under study, as in the methodology developed to obtain reflectance spectra.

It must be taken into account that being an open system several problems could be encountered as a low efficiency. It is highly probable that this acquisition methodology could be improved but it has been decided to test its performance through simple experiments that will be commented briefly.

III.C.2 ANALYSIS ON TRANSMITTANCE MODE OF SIMPLE VITREOUS MATERIALS

In order to test the validity of the acquisition setup previously exposed, some measurements were performed in simple vitreous materials that will act as “models”. The study of chromophores of *tesserae* of stained glass windows is the application of the IS device that could be more appealing. For this reason, the samples desirable were those generally used in such objects and they were provided by Piero and Mattia Modolo from the ancient warehouse of the “Caron Vetrate Artistiche” which are stained glass masters and experts. They are three piece of blue (std 104), yellow (std 186) and red (std 200) glasses from the Saint-Just® [132] used to form *tesserae* of stained glass windows. The samples measure appreciatively 3.8cm x 3.8cm. In order to understand more about the sample composition they were studied by several techniques as XRF, XPS or OM (see Annex 1 for technical details). As an example of these analyses in Figure III.36 some of the data collected are displayed for the blue sample, in particular an image acquired by the OM and a XPS spectrum which shows the main elements that constitute the glassy matrix (Si, O, Na, Ca and Mg). The samples had bubbles in its structure, specially the blue. In fact the OM image in Figure III.36 shows one of these features of the glass fragment.

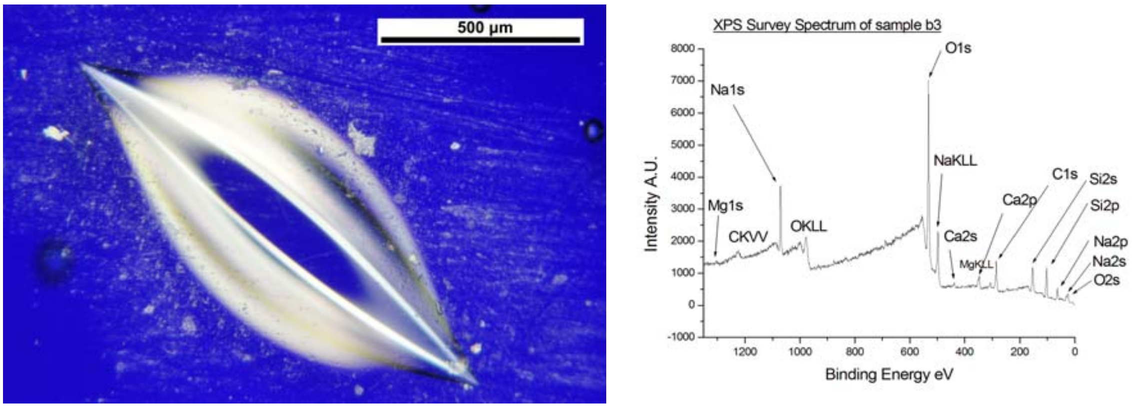


Fig III.36- OM image (left) of a bubble in the structure and XPS spectra (right) of the same blue sample

The samples were used to test the developed setup comparing the data collected employing this methodology with those furnished by the spectrophometer Cary5 (see Annex 1) working in transmittance mode. This was performed in order to control the validity and coherence of the information attained with the IS system. The results will be commented taking into account the spectra quality and agreement between instrument but also in terms of the capacity of the developed device to eventually characterize chromophores of these glass samples.

- Blue glass

In Figure III.37 the spectra obtained by both instruments are compared (In absorbance A=log(1/T)). As it can be observed the data of the IS are in good agreement with those of the spectrophotometer. The shape of the curves and band position are coherent. The spectrum recorded by the developed device is quite more noisy but it is not a critical issue.

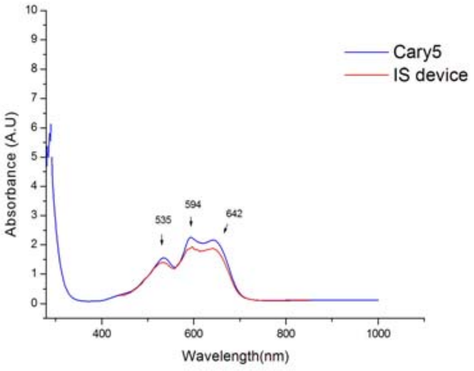


Figure III.37- Spectra obtained by the IS device and by the spectrophotometer of the blue glass

The visible spectra shows the spectral characteristics of the Co(II) in a tetrahedral coordination. The coordination in silicate glasses is predominantly fourfold tetrahedral which rises to the well-known cobalt blue. The UV-VIS-NIR spectra are powerful tools to identify the cobalt. The features at 535nm, 594nm and 642nm corresponds to the strong absorption $^4A_2 \rightarrow {}^4T_1(P)$ [20, 90, 99, 133] and they are perfectly identifiable through the IS system.

- Yellow and Red glasses

In this case, the colour is produced by the band gap or semiconductors type based on the cadmium sulphide-cadmium selenide system. They give yellow, red and orange colouration to the glass. In Figure III.38 the spectra of the yellow glass (left) and of the red glass (right) are displayed.

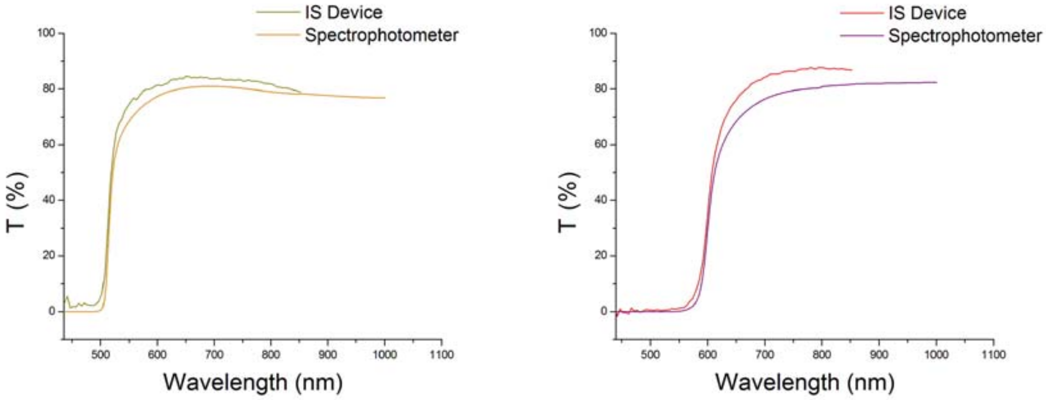


Figure III.38- Spectra obtained by the IS device and by the spectrophotometer of the yellow (left) and red (right) glasses

The spectra reported shows the S shape of these semiconductor colourants. The data of both instrument are in good agreement, the IS curves are more noisy but the quality of the information is adequate allowing to detect the spectral features.

In this case other techniques can be supported by the data furnished by other techniques as XPS or XRF. The latter is able to detect Cd and Se fast and easily, as it has been detected in these samples. On the other hand, XPS spectra of the red sample (Figure III.39) show the presence of Zn. To produce an intense red colouration as the one presented by the sample no sulphur should be added and zinc metal is added in order to reduce the CdO in order to form the Cd(Se)n n≥1 [90]. As it can be observe, the multi-technical approach is useful in order to elaborate robust conclusions, as in this case.

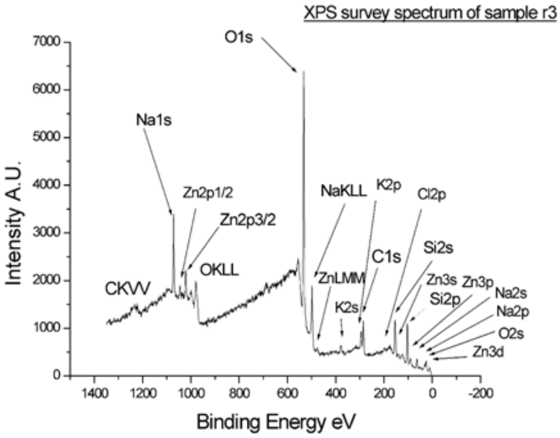


Figure III.39- XPS Spectra obtained of the red glass sample

After the good results obtained, other tests were performed but in this case employing glass samples bigger in order to understand the difficulties that must be faced in these conditions that are closer to the ones that should be faced when studying real stained glass windows. The results obtained where coherent with the data obtained by a Cary 5 spectrophotometer (a piece of glass was cut) and the acquisition setup furnished good results. Afterwards, the possibility to study stained glass windows from the *Capella degli Scrovegni* of Padua offers a challenge for the IS device to demonstrate its application in the field of the study of chromophores in such cultural heritage objects. This part will be discussed on Chapter V. However, the results obtained in this part are encouraging and could represent a measurement modality for transparent artefacts if reflectance mode produce problems.

Chapter IV : Application of IS to the study of mural paintings

The previous chapters have faced essential issues, from the theoretical and empirical point of view. At this point, the developed IS system methodology in reflectance mode was ready to deal with real analytical problems regarding the chemistry for cultural heritage field. Taking into account the characteristics of the instrumentation, in particular the possibility to analyze large size surfaces *in situ*, the application to the scientific examination of mural paintings seems logical. Indeed, IS device was built with these initial purposes.

The first part of this chapter will discuss briefly the elaboration of a spectra database. Its constitution was performed thanks to the production of mural painting replicas. There are some databases available as the previously mentioned of the IFAC-CNR [58]. However it has been decided to create one by measuring specially prepared mock-up paintings with the IS device. The laboratory models had been also measured with a XRF device (see Annex 1) to have additional information. This procedure allowed to acquire these replicas in comparable conditions in terms of illumination, geometry, … with the imaging spectroscopy developed methodology. Moreover, during these measurements it is possible to understand which features are detectable and which not by this technique, fact that could serve as a training for the analysis on a real artwork and to explore the potentialities and limits of imaging spectroscopy. As a precautionary measure, the mock-up painting where also studied by a spectrophotometer (Cary 5, Annex 1) in order to detect any anomaly of the system and if this happens solve the possible causes. The elaboration of such database still is a work in progress. It must be taken into account that the creation of a spectra database is time consuming but it is an operation that results really useful in long terms.

The second part will deal with the interdisciplinary approach for the study and intervention of a real mural painting. The artwork was situated in an office of the Library of the Department of Statistical Sciences of the University of Padua (Biblioteca della Facoltà di Scienze Statistiche. Università degli studi di Padova). The department is located in the former convent of Santa Caterina, which dates back to the XVII century. In particular, this doctoral dissertation will focus mainly on the information brought by the IS system. The study of this mural painting had different objectives, it will be noticed how the IS system contribute to reach these aims. In particular, it will be discussed the benefits of the integration of IS data with elemental information furnished by μ-XRF. The capacity of the IS device to operate *on the field* will be verified, especially when the measurement conditions are challenging.

IV.A Construction of an IS visible reflectance spectra database

The elaboration of a suitable IS visible reflectance spectra database implies the elaboration of laboratories models of the objects that will be studied. In this case, it is necessary to produce laboratory mural painting replicas. These samples must be prepared following as close as possible the techniques and materials used for the elaboration of this artefacts. In order to prepare the mock-ups of an adequate and equal dimensions, a specially designed wood grid was designed that can be observed in Figure IV.1.

Figure IV.1- Wood grid designed to elaborate the painting replicas on the laboratory

The elaboration of the sample was relatively simple using this grid. The painting replicas obtained had a surface of appreciatively 6cm x 6cm, as it is illustrated in Figure IV.2. The third dimension depends on the quantity of *intonaco* and *intonachino* employed to do the mock-up but is from about 2cm.

Figure IV.2- Mural painting replica

In order to elaborate the samples as close as possible, numerous bibliographical fonts have been consulted [67, 68, 113, 134-137] and also restorers have been consulted. As it has been commented in Chapter II, there are three main types of application to execute lime-based wall paintings, according to the drying conditions of the mortar, or more concretely to the degree of the carbonation. The *fresco* technique must be performed while the mortar layer is still damp (but not saturated with wetness). In this phase, the reaction between the $Ca(OH)_2$ of the plaster (that will act as a binder) and the atmospheric CO_2 has not begun. Then, the gas is drawn into the plaster, transforming the calcium hydroxide into calcium carbonate. During this process, platelets of calcium carbonate lock the particles of pigment into the surface of the mural painting. On the other hand, the *secco* technique is applied to the same substrate, but after the mortar layer has thoroughly dried. This procedure requires the use of a binder in the paint as egg or animal glue which then produces a film on the plaster. There is third type of application called *mezzofreso* or *stanco* it is applied when the *intonaco* is in an advanced state of carbonation, pigments will be lock forming a more superficial stratum than in *fresco* technique (however many authors do not considered this third type of procedure). It has been decided to employ the three types of application of the painting to form the mock-up pantings.

The mural painting lime-based replicas were performed in two layers: *intonaco* and *intonachino*. Both layers are formed by 1 part of slaked lime (calcium oxide in solution with water, forming calcium hydroxide) and 3 parts of aggregates (sands or marble dust). The products were provided from a commercial source [138]. The intonaco is slightly more coarse because it has been prepared with 2 parts of different sands (which lead to different colours, *grigio venato*, *giallo di Verona,* ..) and 1 part of marble dust while the intonachino has been manufactured with 3 parts of marble dust. Each mock-up was formed by both layers and a different combination of pigment/application technique. In Figure IV.3 it is reported one of the phases to elaborate some of these laboratories models and in Table IV.1 some of the pigments and of the procedures to apply them on the mural painting replicas are enumerated. More than sixty models were prepared and analyzed, some pigments and techniques are more difficult to execute than others and for these reason the results were not satisfactory (as it has been previously commented, the construction of the spectra database still is a work in progress).

Figure IV.3 – Manufacturing some mural painting replicas

Table IV.1- Some of the pigments and their technique(s) of application to form the mural painting replicas

Pigment and provider	Painting technique
Earth of Siena, local provider	Fresco, Mezzofresco, secco (rabbit skin glue, yolk egg, linseed oil)
Pozzuoli red, local provider	Fresco, Mezzofresco, secco (lime, rabbit skin glue, yolk egg, linseed oil)
Brentonico Green, local provider	Fresco, Mezzofresco, secco (rabbit skin glue, albumin egg, linseed oil)
Ultramarine blue, kremer [101]	Secco (rabbit skin glue, albumin egg)
Nicosia Green, Dolci [139]	Fresco, Mezzofresco, secco (rabbit skin glue, albumin egg)
Natural umber, local provider	Fresco, Mezzofresco, secco (lime, rabbit skin glue, yolk egg, linseed oil)
Prussian Blue	Secco (rabbit skin glue, albumin egg)
Ultramarine violet, Dolci[139]	Secco (rabbit skin glue, albumin egg)
Verdigris, synthesised(Annex 2)	Secco (rabbit skin glue, albumin egg)
Dunkel ochre, Dolci[139]	Fresco, Mezzofresco, secco (rabbit skin glue, yolk egg)

As it can be observed in Table IV.1, different kind of binder were employed when executing the *a secco* technique, the products were obtained from commercial sources [115 ,138], excepting the egg media. In some cases, the mural painting replicas were constructed with more than one layer of colour, in the cases that it was considered adequate. As instance, the azurite pigment was employed on mural paintings applied *a secco* (normally with tempera technique) over a layer of a red ochre or grey pigment previously applied by other painting technique, usually by *a fresco* [134]. With the aim of elaborate the replicas as closer to the artists techniques as possible, several mock-up were prepared for example by painting a *secco* the blue verditer pigment over an *affresco* layer of red to dark colour, as it can be observed on the cross-section OM photography displayed in Figure IV.4 (elaborated with a fragment of the paint layer placed on polyester resin Bascol and then polished).

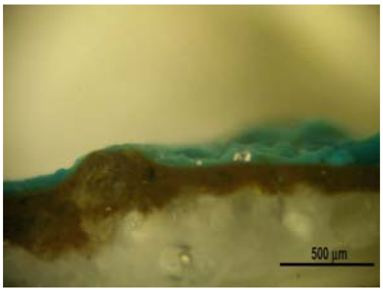


Figure IV.4 – OM view of a cross-section of one of the mural painting

The samples prepared following the previously method described were measured by the IS device in order to collect the reflectance spectra on the range between 420nm and 850nm. For an ulterior verification of the validity of the data furnished, spectrophotometer (Cary 5, see Annex 1) analysis were also performed on the mock-up paintings. The data were in good agreement, the IS data were slightly more noisy and in some cases there are differences in the reflectance values, but as the data obtained in the precedent chapter the developed methodology is adequate. In Figure IV.5 some of the obtained spectra are represented.

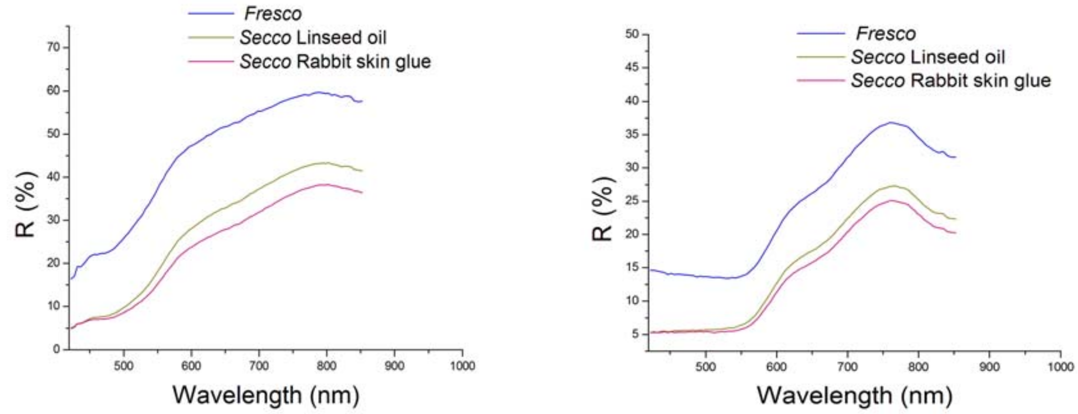


Figure IV.5 – Spectra obtained in some of the mural painting replicas constitute by the Siena earth (left) and Pozzuoli red (right)

Spectra databases are useful tools to identify painting constituents as pigments. In the particular case of this research work, it has been a time consuming part of the work but it has been actually very valuable in order to understand the construction and constitution of these works of art and also of the optical properties of different pigments. Indeed, it has been demonstrated its utility when the IS developed methodology was applied to the study of a real mural painting.

IV.B Application of the IS system to the interdisciplinary study of a mural painting located in the Ex-conservatory *of Santa Caterina soccorso e Gasparini*, current base of the *Biblioteca di Scienze Statistiche* of the *Università degli studi di Padova*

Mural paintings are valuable artefacts that covers the walls of many kinds of buildings. Indeed, Padua is known worldwide for the *fresco* paintings of the *Cappella degli Scrovegni* executed by Giotto di Bondone, simply nominated Giotto. However, in multiple occasions they are in very bad conditions and they must be restored in order to recover at least partially its original appearance.

The mural painting under study was in a really bad conservation state. It was partially covered by several layers of lime plaster and presented also a complex cracking situation. Moreover, from the preliminary observations of the *opera* it seemed that some parts were lost. This artefact was not very remarkable from the artistic point of view but it has been useful to demonstrate the potentialities and limits of the developed IS methodology for the study of such kind of artworks. In particular, the restoration process of the painting was profited to test this instrumentation in the context of an interdisciplinary approach. The dialogue between different experts has been of great importance to reach most of the objectives that were defined before the intervention. In this doctoral dissertation, the usefulness and contributions of the IS device to reach this goals will be discussed.

IV.B.1 INTERDISCIPLINARY STUDY OBJECTIVES

The investigation has involved diverse experts of different fields. In particular restorers, art historians, engineers, and scientists had worked together in order to obtain the better possible outcome. The work was coordinated by the Chemistry of cultural heritage group of the university of Padua. Before start any sort of intervention, the different objectives of this interdisciplinary study were defined as the following ones:

- to understand the state of conservation
- to obtain information on the execution technique/techniques
- to study the painting materials that constitute the *opera*
- to identified the author of the painting and its execution period

- to prove that mobile analytical techniques, and in particular imaging spectroscopy integrated with XRF, can be used in such conditions to study these kind of artworks
- to identify the adequate restoration operations, methods and materials using the collected information

These aims are related one to each other. Information about the execution technique and the painting materials is useful to understand more about the execution period (i.e., the detection of a modern pigment as cadmium red) or to the identity of the author (i.e., use of a particular palette). In order to perform an adequate restoration process it is fundamental to understand which materials forms the opera to recognize any kind of potential alteration or to select an adequate methodology to approach to the artwork preventing incompatibilities. Moreover, the identification of any kind of degradation development is essential in order to stop it and study its causes and solutions.

In this doctoral thesis, it will be discussed how the IS contribute to reach these concrete purposes and if it could be helpful in other issues that were not considered in the interdisciplinary study.

IV.B.2 THE MURAL PAINTING

The artwork under consideration is located in a little office (approximately 7.17m of width, 3m of length and at a height of 4.8m) of the Library of the Department of Statistical Sciences of the University of Padua (Italy) (*Biblioteca della Facoltà di Scienze Statistiche. Università degli studi di Padova*). However, this building which date back to the XVII century has been used for other purposes. Since the year 1627 *circa* the complex hosted the nun order of *S. Maria Maddalena delle Illuminate* until the XIX century when a Napoleonic proclamation suppressed the religious corporations. From then, the convent has been transformed to pious conservatory and for other similar charity institutes. Finally, in the year 1997 the Library of the Department of Statistical Sciences has occupied the complex [140].

The room where the mural painting is placed has not always been of its current modest dimensions. In fact, different documents acquired from archival fonts has indicated that previously the space was wider and has been used as a refectory or as a chapel as it can be observed in Figure IV.6 [141].

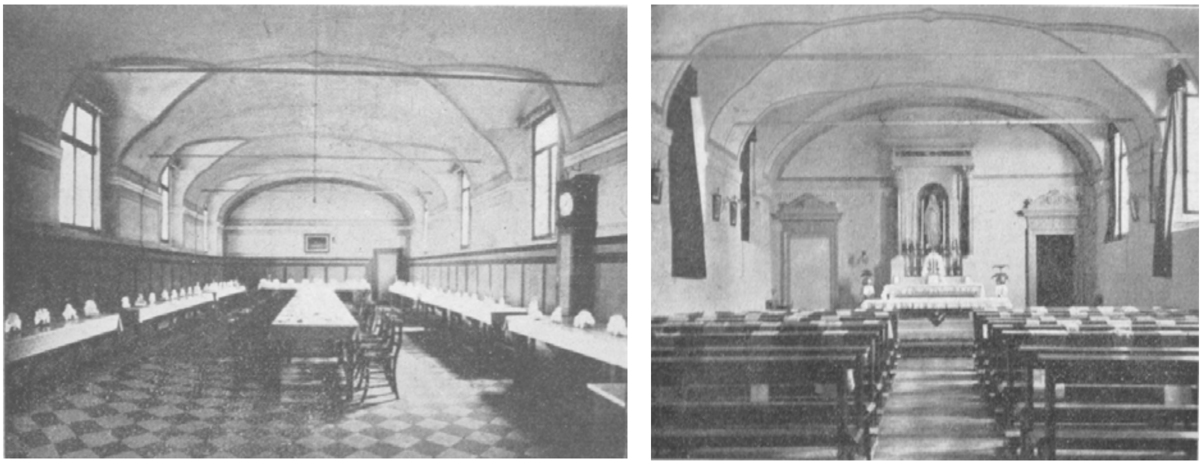


Figure IV.6 – Pictures of the room where the mural painting is placed documenting its different uses and structural modifications. In the left a photography of indeterminate date of the end of the XIX or beginning of the XX century when the space was a refectory. In the right part a picture of 1931 where it can be observed that the room was a chapel

In the reported pictures the mural painting is in the upper part (in particular in the half-moon structure above the door) of the opposed wall. The artwork is not visible because it is covered by different lime-plaster and painting layers. Moreover, in the photo of 1931 it can be seen that the upper part of the altar is blocked in its central part [141].

When the study begun, the mural painting presented very bad conditions. It lies over the entrance door of the office, which is placed in the central part (where in 1931 was the altar, see Fig. IV.6), and it is 7 m wide and 1.8 m tall at its highest point. As it has been already commented, it was partially covered by successive layers of plaster and painting, and presented structural defects, especially in the central part above the entrance. Probably these cracking situation was a consequence of the altar that was placed in this position as it can be observe in Figure IV.6. The artist is unknown, but it is thought to be a minor member of the Paduan school of the time. The work of art is organized in different scenes, one in the central part and another on its laterals. At both sides, it is represented an Annunciation episode with the Virgin on the left and the archangel Gabriel on the right. The central portion illustrates a passage that could be either a Last supper or a scene of the life of Saint Catherine in particular the discussion between the Saint and the philosophers (*Disputa tra Santa Caterina d'Alessandria e i Filosofi)*. Later, when the restoration has recovered some parts of the mural painting, it has been identified as a last supper representation. Through the observation of the iconography, it was possible to date the artwork from a period between the XVI and the XVIII. In Figure IV.7, some details of the central part and of the right section are reported in order to show the conditions presented by the *opera* before the restoration process.

Figure IV.7 – Part of the central scene (left) and of the right portion (right) of the mural painting before the restoration process

The main phases of the restoration process includes a first phase aimed to the removal of the lime-plaster and other layers which cover the artwork, following by different consolidating operations in order to secure the paint film avoiding the lost of the remaining *intonaco* stratum and providing stability to the structure. Then, the surface was cleaned employing different products as surfactants. These first procedures will be nominated “cleaning phase”. After the elimination of the covering layers, some figures indicating the execution period have appeared in the central part of the ornamental frame of the artwork. They are “M D C X … “ indicating that the artwork dates back to the XVII century. The possible intervals are from 1610-1649 or between 1690-1699. So, one of the aims of the interdisciplinary study has been partially resolve. It will be difficult through the scientific examinations to define more precisely this interval.

When the cleaning phase was concluded, the wide portions that had been lost, in particular in the central scene, needed to be filled with neutral lime-plaster layer of a colour and thickness in harmony with the *opera*. Then, some tiny missed parts of the paint film has been retouched. All these operations, were nominated “retouching phase”. In Figure IV.8, a photomosaic of the different phases of the restoration process performed by Arcadia Ricerche [142] is showed.

Figure IV.8 – Photomosaic of the mural painting during the different phases of the restoration process

IV.B.3 NON-DESTRUCTIVE EXAMINATION WITH MOBILE TECHNIQUES

In order to study this mural painting, different techniques were employed selected for they ability to give complementary information as photography in normal and ranking light in the UV and visible range or termographic measurements. However, the most important from the point of view of the chemistry for cultural heritage are the mobile techniques μXRF and IS.

Both techniques have been employed to the study of the mural painting in two measurements campaign, at the early stages of the restoration process and when the work was concluded. In particular, the μXRF were executed before the beginning of the restoration and when the intervention was completely finished. IS measurements were performed in a first campaign after the cleaning phase and then when the retouching phase was completed. The results collected with both instrumentation was discussed with the components of the interdisciplinary study in order to reach the maximum fruition and accomplished the aims that had been defined. Indeed, it is vital to decide with the different experts, especially with art-historians and restorers, the part that must be analysed. In fact, μXRF is a spot technique so in order to do not lost valuable measurement time (usually in this kind of measurement the access to the artwork is limited!) it is highly advisable to plan the points to analyzed. IS technique from this point of view has presented an important advantage because the developed methodology permit the acquisition of a wide region of interest.

It must be taken into consideration that the conditions *in situ* are not the stable and known environment of a laboratory. In fact, in order to reach the painting a scaffold was necessary and that render non totally steady the positioning of the instrumentation. Moreover, the restoration process implies also a dust problem because this material can be accumulated inside the different components of the devices or of the computers that can produced different problems as the broadening of the XRF peaks. In the particular case of the IS device, it is normally supported on a tripod that had to be disassembled to perform the measurements and was positioned on other support (a metallic base). The experimental conditions avoided the acquisition of many points with the μXRF and of the most lateral section with IS instrumentation. It can be said that from this point of view the developed system was more versatile and permitted the acquisition of more section of the painting than the commercial μXRF device. In Figure IV.9 the experimental conditions employed for the study with both instruments are showed.

Figure IV.9 – Experimental setup adopted for μXRF (left) and for IS (right) analysis of the mural painting

In this conditions, the μXRF (for more technical details see Annex 1) measurements was non provided with He purging. For this reason, the elements with Z >18 are easily detectable, those with 13< Z < 18 are detectable but the equipment is not capable to detect elements lighter than the Si, Al and Na as instance. The measurements were performed with a collimator with a diameter of 1mm. In each analysis campaign, about 50 spots were examined through this technique and it required approximately four days, before the restoration and when it was concluded. On the other hand, IS measurements must be performed during the nights to avoid the light coming through the big windows and the transparent door. The time required was two nights by campaign. Thanks to this technique, almost the totally of the painting surface was studied, only the most exterior parts were not acquired. In fact these is another advantage of IS technique if it is compared with μXRF, the large amount of data that are recorded considering similar time at disposition. It must be said that in these conditions, most of the time of fluorescence measurements was employed in the positioning of the instrument, that had to me moved from point to point whereas the IS was also difficult to be adequately placed but in one shot it recorded entire regions and not spots. However, the large amount of data could be difficult to handle and elucidated afterwards, but with the developed methodology a good compromise had been reached.

The IS measurements were performed following the developed measurement methodology but applying them to the particular conditions of this *in situ* analysis. In order to achieve the most uniform illumination of the scene, the acquisition setup consisted in two halogen lamps and two metallic iodide lamps, placed at approximately 45° with respect to the painted surface. The artwork was too wide to be scanned in a single acquisition, so separate measurements were performed in each campaign. With regard to the reference white, the standardized panel was not sufficient to cover some of the sections. Therefore the white signal was acquired in different steps, placing the reference in different, but partially overlapping, positions. In one of the scanned regions, in addition to the white panel a 1% PVA/ $BaSO_4$ paint film deposited on a glass support was used to verify the utility of this standard specially prepared on the laboratory, as it has been already commented on Chapter III. For the first campaign, the annunciation scene of the mural painting was studied by two measurements from a distance of 3 m with an angular step of 0.25 mrad, giving a spatial resolution of less than a millimetre. Two acquisition were required to study the last Supper that have the same resolution as they were performed at half the distance but with double angular step with respect to the former ones. In Figure IV.10 two (R, G, B) reconstructions of the acquired regions of interest are showed.

Figure IV.10 – (R, G, B) reconstructions obtained with the IS device of two of the regions of interest of the mural painting of the annunciation scene (left) and of the central part (right)

In the second campaign, the operating conditions were similar that for the first one. The only difference was that in some of these acquisitions it was decided to obtain the data with the IS device with a better spatial resolution. In Figure IV.11 three (R, G, B) reconstructions obtained from the data collected by Imaging Spectroscopy during the second campaign of some regions of interest are reported.

Figure IV.11 – (R, G, B) reconstructions obtained with the IS device of three regions of interest of the mural painting of a window of the annunciation scene (left), of a personage of the last supper (central) and of a detail of the Saint Gabriel (right)

As it has been previously mentioned, from each pixel of these (R, G, B) reconstructions it is possible to obtain the reflectance spectra on the range between 420nm and 850nm. In this particular study, the main information that could be extracted is the characterization of pigments, and its spatial position over the surfaces acquired. This information is essential in order to understand the execution technique of the painting. Moreover, it is useful to determinate the period of elaboration of the artwork and the possible identity of the artist, or at least learn more of these aspects. The knowledge of the materials that constitute an object under restoration is really valuable. In this manner, it is possible to evaluate possible risks of each kind of system and select the adequate materials for the intervention in order to prevent undesirable consequences in the future.

The analysis of the first campaign provided information about the basic palette of the unknown artist whereas from the data of the second it was possible to test if the IS system was able to detect the retouching pigments applied in the restoration process. The results will be presented divided in colours or group of colours of the original palette with a separate section for the data collected regarding retouches. The reflectance curves that will be commented are "raw" which means without any smooth operation that could be applied but the purpose is to show the original IS data. The only elaboration performed was an average of some neighbouring pixels as it has been already explained for the development of the measurement methodology The information discussed will deal essentially with the spectra furnished by the imaging spectroscopy approach, the μXRF will be considered as a tool to verify the conclusions and to demonstrate the benefits of a multi-technical approach based in this two mobile instrumentation.

<u>IV.B.3.A Red and Yellow areas</u>

These colours are presented in many areas of the mural painting, as in the dresses or in the flesh of the personages. In Figure IV.12 some of the spectra of these regions are displayed.

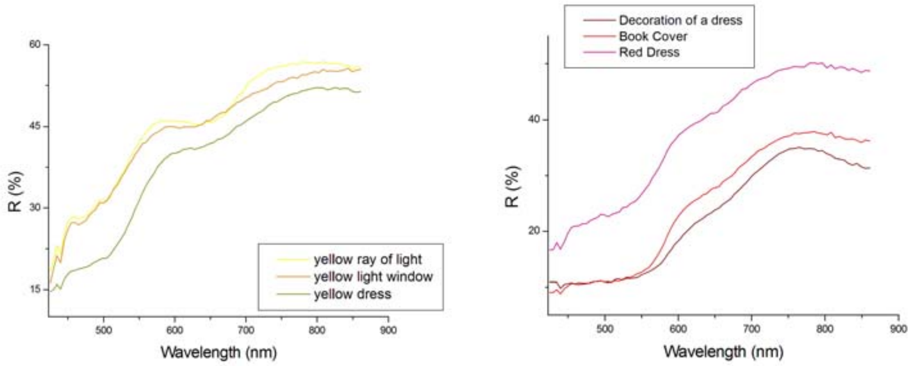


Figure IV.12 – Spectra obtained in some of the mural painting yellow (left) and red (right) areas

From the obtained spectra it is possible to conclude that the employed yellow and red pigments are natural earths. Earthy pigments with a yellow to red colouration are usually called ochres even though in pigment terminology the word could be used as a synonym of yellow ochre. Its colour is given by a presence of different iron oxide hydroxides and oxides, mainly goethite α-FeOOH and hematite α-Fe_2O_3. They have been used as pigments since the prehistoric times. In the XIX century, the chemical industry produced the synthetic version of these compounds (Mars colours). However, they have never fully replaced the natural ochres. When the hematite is the main iron oxide the colour of the pigment is red whereas it is yellow when the goethite dominates. These materials could also be brownish due to the presence of manganese oxide. Observing the spectra obtained for the yellow areas, they are characterized by sharp positive curves with an inflexion point within the interval 539nm and 550nm whereas the pure goethite is situated at 550nm. On the other hand for the red areas, the spectra show also a sharp slope at around 580nm as the pure hematite [103, 106, 143, 144].

The main cause of the colour of these pigments is the ligand to metal charge transfer transition that produces in both hematite and goethite a strong absorption in the UV region as it can be noticed in the spectra of Figure IV.12. It must be recalled that these bands are very intense because they are permitted. In fact, the reflectance curves show other weaker features that are produced by the Fe(III) $3d^5$ Oh in high spin configuration that are Laporte and spin forbidden. For both colourations it is possible to detect in the spectra reported a weak absorption at around 649nm which corresponds to the transition $^6A_{1g} \rightarrow {}^4T_{2g}$. In addition to these characteristics, it is possible to notice that in the reflectance of the yellow regions of this mural painting (Fig. IV.12 left) there is another band at around 477nm which corresponds to the pair transition $2(^6A_1) \rightarrow 2[^4T_1(^4G)]$ and at 434nm a feature is produced by the $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_{1g}$ transition. This last mark is not so clear in the IS data because it is at short wavelengths and this can produce difficulty in its identification. The same problem is found to notice this band on the red areas of the painting (Fig. IV.12 right) where the $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_{1g}$ transition is situated at 444nm. In the spectra corresponding to this colour it is possible to observe the pair transition $2(^6A_1) \rightarrow 2[^4T_1(^4G)]$ at 529nm [103, 106, 143, 144].

The present discussion demonstrate the utility of the IS methodology to characterize pigments. In order to verify the identification that has been performed of the experimental data of the

S.Caterina mural painting, a comparison was performed between the red and yellow regions acquired from this artwork and from the spectra database constructed that are displayed on Figure IV.13. The spectral curves of these coloured areas of the paintings are in good agreement with the earthy pigments Pozzuoli red and Siena ochre applied with the *fresco* technique of the built database.

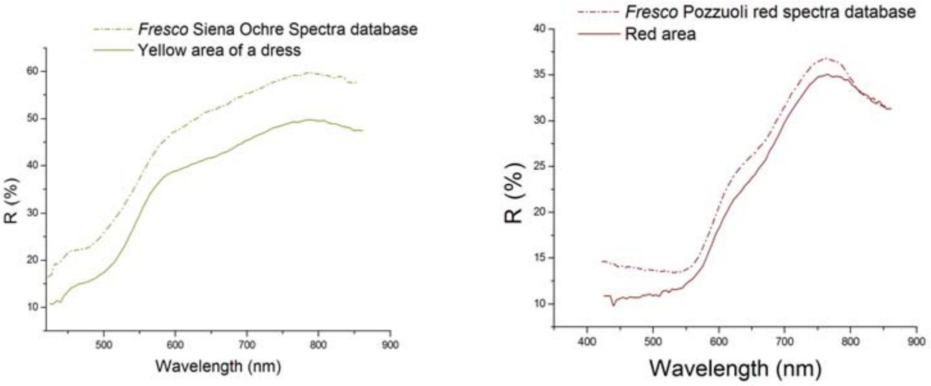


Figure IV.13 – Comparison of the reflectance curves obtained with the IS system in some of the mural painting yellow (left) and red (right) areas with the spectra of the built database

The μXRF data support the conclusions obtained with the IS developed device because the main elements detected on these areas are Ca and Fe.

There is one particularity in one of the yellow regions of this mural painting. The area is one of the shoulders of a central personage. Its reflectance curve does not present the features of the yellow ochre previously discussed. Its reflectance spectra obtained with the IS device is compared with the typical curve of the other yellow area on Figure IV.14.

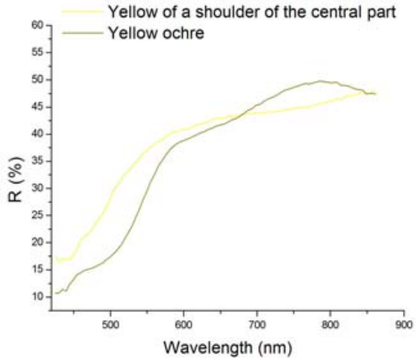


Figure IV.14 – Comparison of the reflectance curves of the yellow ochre and the other yellow pigment employed on the shoulder of a central personage of the mural painting

The S shaped spectrum observed in this particular yellow area is due to a band to band transition, in particular to a lead based yellow pigment. The colouring agent could be lead-tin yellow, term of modern invention referring to two lead tin oxide compounds, the so-called “type I” of composition Pb_2SnO_4, while “type II” contains silicon in the crystal lattice to give a compound of approximate formula $Pb(Sn_{1-x}Si_x)O_3$, with $x \sim 1/4$. The term may also encompass tertiary compounds based on Pb, Sn and Sb. On the other hand, the pigment producing such colouration could be Naples yellow, that refers primarily to $Pb_2Sb_2O_7$ although other tertiary lead antimony oxides with tin and, to a lesser extent, bismuth and zinc, can be found. The latter typology of pigment has been used since antiquity times while the use of lead tin yellow has been identified in painting dating from 1300 to 1750, however it could have been use before this period. Both are relatively stable to the mural painting media. In this case, it is difficult through the IS data to state which pigment produces the colour [22, 104, 73-76]. Moreover, the XRF spectra shows the presence of Pb, Sn and Sb as it can be observed in Figure IV.15.

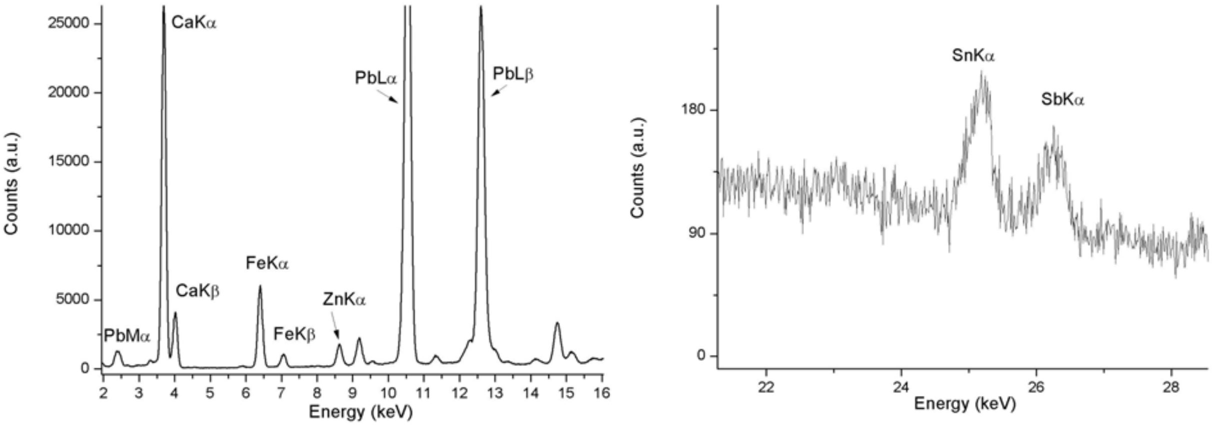


Figure IV.15 – XRF spectrum obtained for a yellow area of a personage of the central part, general view (left) and detail of the Sn and Sb signals (right)

Taking into consideration the collected information, it is difficult to affirm which particular pigment has been used. The Sn signal has been detected in several spots analyzed by XRF, so it could be hypothesized that particular label of this yellow are Pb and Sb, that could indicate that the most probable pigment used in this region of interest is the Naples yellow. However, it is not possible from the collected non-destructive data to deduct which of the probable compounds has been used. It is also possible that the pigments where used together, or that the Sn detected in the other spots was an impurity of the brush, …. However, it is interesting the use in this particular area of the mural painting of this different yellow pigment. They are two main possible hypothesis, the first one is that to execute this scene of the artwork (where most part of the *intonaco* has been lost) the painter used a different material because this scene was considered most important than the lateral. The other option is that the painting was elaborate by two artists that could employ a slightly different palette. In fact, from the analysis of the *opera* realized by some experts of the interdisciplinary study, it is possible to distinguish two different styles in the execution technique that support this supposition. However, it was not possible to verify this hypothesis. The important conclusion regarding the potentiality of the IS developed methodology is that it has been able to distinguish between the two different yellow regions of interest. It had permitted the clear identification of the earthy pigments based on hematite and goethite. Moreover, the IS spectra completed with the XRF data allows the classification of the secondary typology of yellow pigment as a lead-tin or Naples yellow.

IV.B.3.B Blue and Violet areas

Blue and violet colouration is present in some areas of the mural painting, as in the Virgin dress, in the angel wings or in the clouds. In Figure IV.16 some representative spectra of these regions are reported.

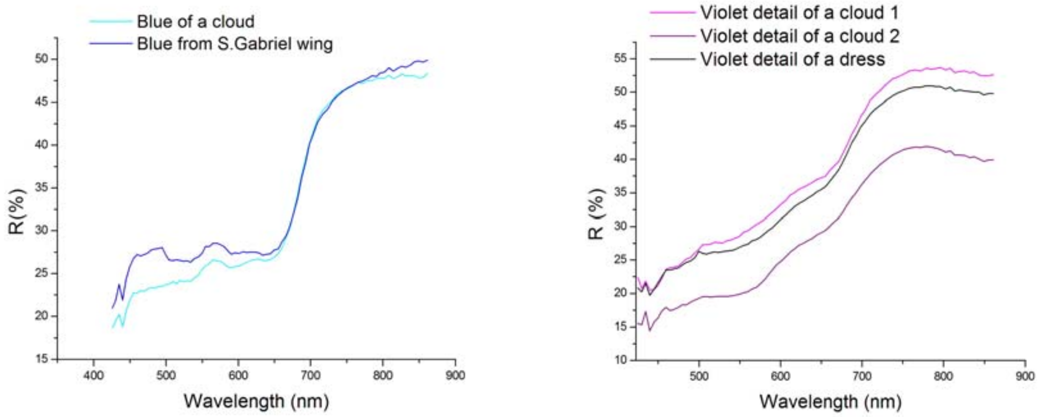


Figure IV.16 – Reflectance curves obtained with the IS system in some of the mural painting blue (left) and violet (right) areas with the spectra of the built database

The main features present in both blues and violet areas are the absorption due to the Co(II) in a tetrahedral coordination that can be observed at around 544nm, 590nm and 649nm. The band centred at ~ 600nm is composed by three subbands that are a consequence of the Jahn-Teller split for the d^7 Co(II) $^4A_2 \rightarrow {}^4T_1(P)$ [1, 17,20, 90, 99, 133].

It must be taken into consideration that pigments in real mural paintings as this one are applied generally mixed between them, and in some cases with charges. Moreover, if the technique employed was a *fresco* or *mezzofresco* the *intonacho* has some colouration that contributes to the reflectance spectra. In fact, in this case it has been observed how the lime-plaster layer had a some kind of yellowish-greyish hue, that was not a bright white. For this reason, the interpretation of the spectra at first could seem difficult. However, a closer analysis of the recorded reflectance curve allows to identify the blue pigment used as smalt, a coarsely ground potassium glass containing Co(II) that produces its intense blue colour. The use of this colouring material was introduced in Italy in the late Middle Ages and was widely used because it was less expensive than other blues as the ultramarine. Its employment decreased with the introduction of synthetic products as Prussian Blue [15, 17, 73, 75].

To obtain the violet colouration, there are two possibilities. Use a compound of this colour as the cobalt violet or to mix a red and blue pigments to produce such hue. The cobalt violets (see Table II.1) are synthetic products that had been introduced from the XIX century, so they could not have been used in this mural painting. Moreover, they present a different VIS spectra if compared with those of Co(II) in a smalt pigment. From the spectra in Figure IV.17, it is possible to identify the latter compound, so the violet has been produced by mixing a blue smalt with a red pigment. It has been already commented that it has been used a red ochre in the areas of this colouration of the mural painting. Then, it seems probable that the artist had employed a mixture of smalt and red earth to produce the violet hue. However, this hypothesis must be verified by the scientific data, because it could have been used as instance a red lake pigment that is not detectable with the XRF data. In order to verify that the production of the violet colouration was a mixture made by blue smalt and a natural red earth, the characteristics spectra of a blue and red region of the mural painting where added. The obtained spectrum was compared with the reflectance curve of a typical violet area of the artwork. The calculation of the effect of pigments mixture on a paint is normally calculated by means of the Kubelka-Munk theory and this is not a trivial issue, especially in the cultural heritage field [18]. However, the objective of the elaboration adopted was absolutely qualitative and used as “indicative” and for this reason a simple addition has been used instead of a more appropriate method. In Figure IV.17, the blue and red spectra characteristics of this mural painting has been summed and the result of such operation has been compared with the typical spectrum of a violet colouration founded in the artwork. It can be noticed that the correspondence between both calculated and the real reflectance curves is good if the shape, which means the bands position are considered. From these evidences, it can be affirmed that the violet employed in the mural painting was created by mixing red earth and blue smalt pigments. The difference in the reflectance value does not mean an incongruence because it could be produced by the addition of a white pigment as instance.

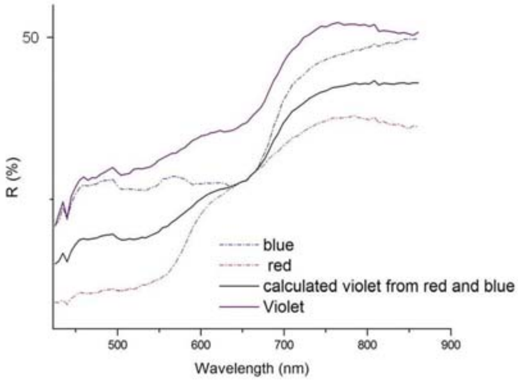


Figure IV.17 – Comparison between the spectrum of a violet region of the painting with the reflectance curve obtained from the addition of a red and blue characteristics spectra founded in the artwork

The XRF data support the conclusions extracted from the IS information. In both blue and violet areas it has been found the presence of the elements K, Co, Ni and As as it can be observed in the information reported in Figure IV.18.

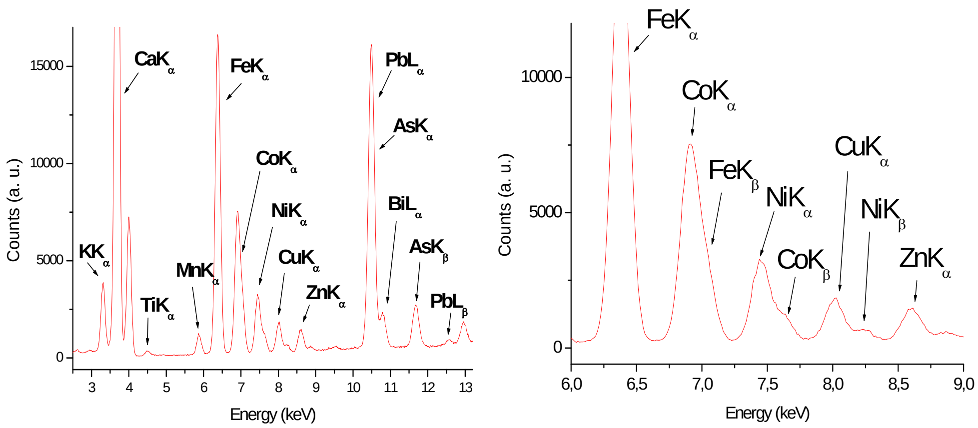


Figure IV.18 – XRF spectrum obtained for a representative blue/violet area of the mural, general view (left) and detail of the 6.0-9.0 KeV range (right)

The presence of Ni and As is an evidence of the preparation of the glassy pigment from cobalt minerals such as skutterudite, $(Co, Ni)_x As_{3-x}$, or cobaltite, CoAsS. These raw materials are firstly roasted and then melted with quartz and potash, but the treatment employed with not efficient heating technology is not effective in removing the As. The presence of K is a further confirmation of the presence of the smalt [15].

IV.B.3.C Green areas

There are some areas of the mural painting with green regions as some part of the wings of the angels, some unidentified objects or some decoration of the angels dresses as medallions or belts.

From the IS information collected, it is possible to differentiate two green pigments that had been used to create this colouration in the mural painting.

The first one seems more darker and it is present in different areas of the painting as in some unidentified objects beside the Virgin or in some details of the dresses. The characteristic spectrum of such regions is showed in Figure IV.19.

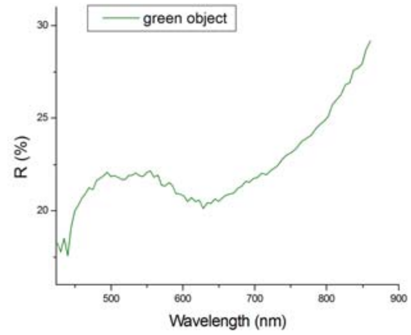


Figure IV.19 – Characteristic reflectance spectrum obtained by IS of a green area of the mural painting

The spectra obtained for these green areas allow the identification of the pigment as a green earth with a broad reflectance band with maximum from 490nm to 540nm. There are different bands in these spectra that produce the colour but mainly they could be described as a result from a strong charge transfer absorption in the near-UV and a superimposition to the latter of several ligand field and intervalence charge transfer (Fe(II)/Fe(III)) transitions. The features of the collected reflectance data with a slight shoulder on the short wavelength and a slightly higher reflectance values in the red region identify the green pigment as a green earth [105]. Some of the main characteristics of this kind of pigment has been already commented in precedent chapters of this dissertation.

The mural painting presents another typology of green pigment that has been found in some "precious" decorative details of the angels, as in belts and medallions. Nevertheless, these portions showed a paint film more damaged if compared with the other parts of the artwork. Unfortunately, the IS spectra obtained of these regions do not bring a clear conclusion about the pigment identity. The reflectance curves are different from the ones presented by the zones where the green earth was employed, but there was not a clear feature that allows the characterisation of the colouring agent employed. This can be due to the damage conditions presented by these areas. However, from IS data it could be deduced that the pigment is non a green earth which lead to multiple solution. In this case, the XRF information is fundamental to a better understanding of the green pigment used in these regions. In Figure IV.20 the area analysed and the XRF spectrum of the second typology of green pigment are displayed.

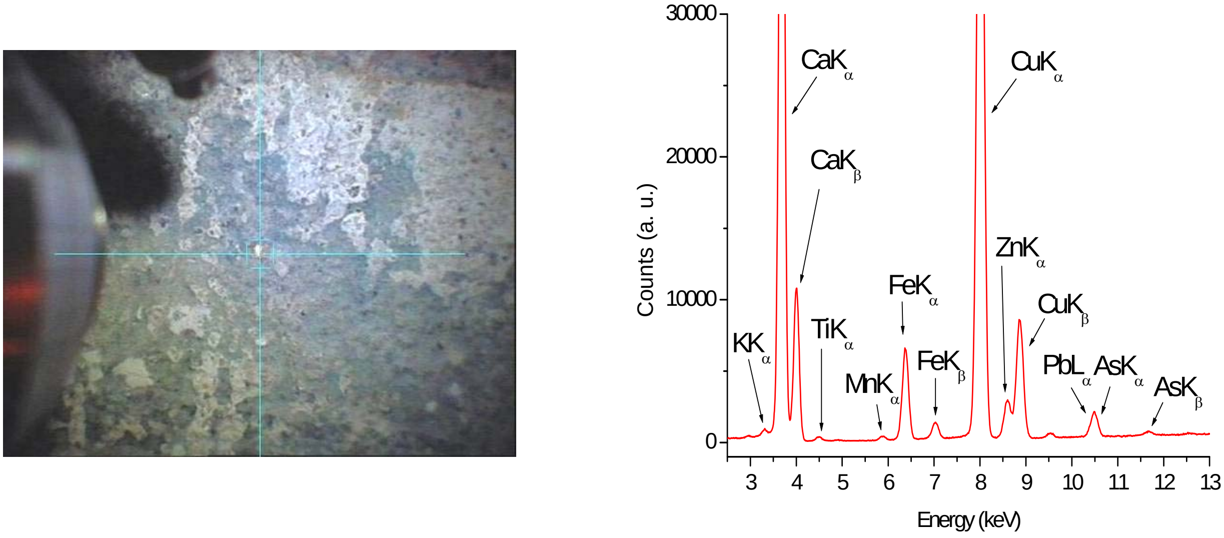


Figure IV.20 – Region analyzed (left) and XRF spectrum (right) obtained for a green decoration in an angel medallion of the mural painting

The XRF data had clearly detect an intense signal produced by the Cu, so this green is produced by a copper base pigment. Unfortunately, there are many compounds that can be used as the verdigris or the malachite. The latter has been frequently used in mural paintings. However, with the IS and XRF information the only conclusion that can be reached is that this green pigment is different from the green earth and that is a copper base compound. Additional analysis with a invasive technique or a Raman portable device could bring additional information that could have finally identify this pigment.

IV.B.3.D Retouched regions

The IS analysis performed after the conclusion of the restoration process was able to differentiate some of the materials employed in some retouched tiny areas. In order to understand the difficulty of this operation, it must be taken into account that these zones are so modest that for a no skilled eye (as the one of a chemist!) they are not appreciable. The expert restorers and art-historians had practice to distinguish such retouches, but is not a trivial operation if the intervention has been executed satisfactorily.

In some cases, the differentiation cannot be performed as for the yellow retouches, because the colour employed was the same as the original (which product could be better!). However, in some other circumstances it has been possible to detect the inpainting by the developed IS methodology, which is a very encouraging result that illustrates the potentialities that could represent the technique for the chemistry of cultural heritage field, especially for a non invasive multi-technical approach.

In Figure IV.21 a retouched and original green details of green regions of the painting are indicated on the (R, G, B) reconstruction obtained with the IS device together with the obtained spectra of both areas and a reference of the Cr_2O_3 pigment.

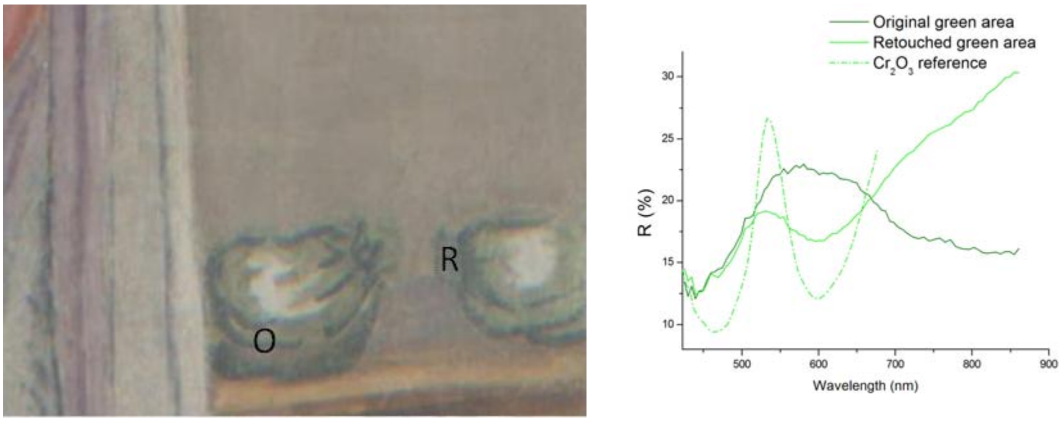


Figure IV.21 – (R, G, B) reconstruction (left) obtained with the IS device with the two areas original O and retouched R indicated and the spectra (right) of these area and of a pigment reference

It is clear from the spectra of Figure IV.21 that from the data obtained with the IS device it Is possible to differentiate the original from the retouched green pigment. In particular, the material used by the artist is a green earth because the reflectance curve presents its typical features previously discussed. On the other hand, the modern material employed to do the retouches is Cr_2O_3, that could be identified from the typical absorption bands at 460nm and 600nm corresponding to the transitions $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ respectively produced by Cr(III) in a d^3 configuration. This is confirmed by the Cr_2O_3 reference spectra. So, the IS analyses allows not only the differentiation of the green retouches but also the identification of the no original pigment.

The IS system permitted also the differentiation of some red retouches as it has been highlighted in the comparison of the reflectance curves of an original and a retouched red areas of Figure IV.22. In this case the difference is less evident than for the individuation the green retouches. However, the reflectance spectra collected by IS still allows its differentiation. Indeed, in the characteristic spectrum of the material used on the red inpaintings the features of the red earth are not present, as the absorption at ~649nm. In addition, the original has a maximum on the reflectance curve at near 770nm and then the reflectance decreases, while the retouched pigment is characterized by a S shape that does not present this behavior. The pigment is the red cadmium $CdSe_{1-x}S_x$ a semiconductor pigment characterized by this shape. Its identification is not straight only by the visible spectra [30]. Nevertheless, its employment seems highly reasonable from this information because the use of cinnabar that has a similar reflectance curve does not seem a feasible option nowadays. Moreover, the XRF spectrum of a restored area of this colour has detected the signal of Cd and Se. The integration of both portable technique allows a robust differentiation and characterization of the red retouches.

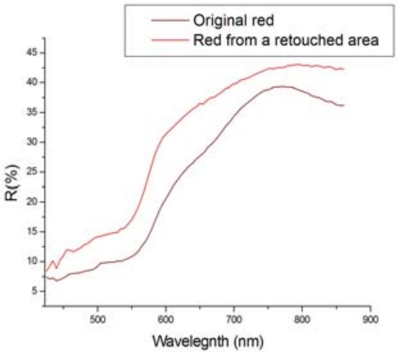


Figure IV.22 – Comparison of the obtained IS spectra of an original and a retouched red areas

The differentiation of the blue retouches had resulted more difficult than the latter cases. In Figure IV.23, a comparison of the reflectance spectra obtained through IS of an original and a restored blue area is displayed.

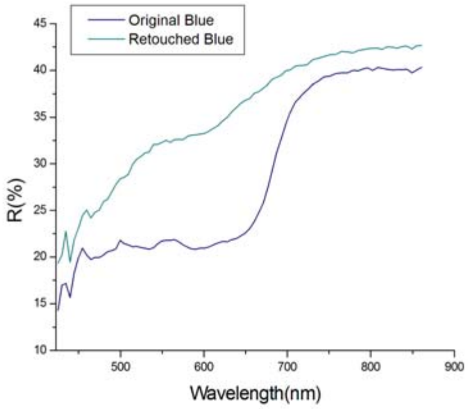


Figure IV.22 – Comparison of the obtained IS spectra of an original and a retouched blue areas

As it can be observed in the reported comparison, the original and retouched areas are different and imaging spectroscopy is able to detect this dissimilarity between the original and no original blue pigments. However, from the spectrum characteristic of these blue retouches it is difficult to individuate a particular blue pigment. It can be said that is not smalt because it does not present its typical features. In this case the, the XRF information does not provide a too specific complementary information which allow to conclude the nature of the compound under consideration, because the pigment used was the Prussian blue. The Fe is the typical element of this colouring agent but in some conditions is not straightforward to identify the retouching material. The Prussian blue has a reflectance spectra with a strong absorption from 400nm to 1000nm, but in this case it must be taken into account that in order to regulate the colour of the just hue, different components are added to a mixture that interferes the reflectance data. The IR range could result useful to identify this pigment. However, IS allows the differentiation of both blues even though it does not fulfill all the analytical expectations.

IV.B.4 CONCLUSIONS OF THE INTERDISCIPLINARY STUDY OF THE *S. CATERINA* MURAL PAINTING

From the results reported, it has been demonstrate that the developed IS methodology is able to collect visible reflectance spectra with sufficient quality on very large surfaces of mural paintings.

The interpretation of these spectra allows the clear identification of some pigments. In this case red and yellow ochres, smalt and green earth has been detected. Moreover, through the IS data it has been possible to conclude that the violet colouration was produced by mixing red earth and smalt. The developed system has also recognized some retouched green, red and blue areas, but it has only been able to identify the pigment employed in the green and red cases but not for the blue restored areas. The integration of this technique with the μXRF information offers a non invasive transportable approach of interest for the study of such type of artworks. In many cases, the detection through XRF of key elements can support the conclusions reached from the IS spectra and complete this information in some cases as in the reported case of the copper base green pigment or for the red retouches. Moreover, it must be taken in consideration that the VIS spectra gives information from the colouring layer whereas the X Rays are more penetrating and furnishes also data coming from more intern stratums. With the IS technique other colours as black and white have not been commented because the spectra where not significant. For the used black, its organic nature made it unsuitable to being detected through XRF but from some clear spot analysed it was possible to identify the white as a calcium white (due to the high signal of this element) as the San Giovanni white. The two techniques present advantages and disadvantages, the aim is to obtain the major fruition by its integration. They have demonstratde to be able to work in the difficult conditions of a restoration site giving good results.

The interdisciplinary study was aimed to accomplish some different purposes. IS technique has importantly contributed to reach this goal. Knowing the pigments is a key point to investigate the author, period and technique of execution. The painter is retained to be a minor member of the Paduan school of that time. The period of elaboration has been defined by the figures “M D C X…” (Figure IV.23). Unfortunately it was not possible to refine such interval of time trough scientific or archivist research. The execution techniques have been partially described by this non invasive approach. From the IS and XRF data, the author or authors palette has been mostly defined. In order to determinate some still unknown aspects as the identification of the copper base green or black pigments another technique(s) are required. To determinate if the painting was applied with *fresco*, *mezzofresco* or *secco* and in this last case identify the binder, another methodology is required because neither IS nor XRF information could help to deal with this issue. The visual examination observations made by restorer and art-historians experts suggested the employment of the *fresco* technique. In fact, the comparison with the spectra database (Fig. IV. 13) were performed with the fresco references because they provided the best matched results. However, the IS developed methodology do not provide so refined information and this fact must not be taken into consideration. In fact this is one of the most important limitations of this approach. In order to understand these issues, it is usually required a invasive method that will allow the observation of the cross-sections of the areas. Some research groups are working on the identification *in situ* but it is a difficult procedure [136]. On the other hand, the non invasive approach was helpful to understand which materials and methods were adequate for the restoration process. This was also deeply influenced by the fluent dialogue between the different competences. As it can be noticed, the aims were almost accomplished. The general conclusion of all the interdisciplinary teams was positive overall.

Figure IV.23 – Figures on the mural painting that indicates its elaboration period (XVII century)

The IS data cube contains information in both dimensions, spatial and spectral. In this work, the information has been presented divided in colours to define the artist palette. However, additional elaboration of the hyperspectral cube could furnish a more visible representation of the data. This is a future perspective of the work that could increment the analytical power of the IS system but for the moment the aim was to demonstrate its potentialities, limits and reliability as in fact it has been done. The device was also employed for some tests regarding the selection of the neutral colour that should be used to fill the multiple and big *lacunae* of some parts of the mural painting, mostly of the central part. Actually, the IS measurement has been used as a tool for the selection of the adequate hue to be used in these lost parts. These applications, together with the possibility to monitor the artwork in time (if there is the possibility) and to store and manage all the data collected are other potential and interesting applications of the IS technique regarding the study of mural paintings.

Chapter V : Application of IS to the study of vitreous objects

In chapter III the IS device has been used to study vitreous objects in transmittance mode. The employed device was built in origin to acquire reflectance spectra in the visible range. However, the IS instrumentation can be adapted to perform transmittance measurements by modifying the acquisition setup. The changes necessaries in order to record visible spectra in this alternative modality for transparent samples are not demanding, almost all the components required are also used in reflectance mode, except for the diffuser. The results obtained during the tests performed to verify the reliability of the transmittance methodology that had been previously discussed in chapter III were quite encouraging. Taking into account these considerations, it is possible, with some instrumental components at disposition, to study artworks in both reflectance and transmittance mode adapting the instrumentation to the analytical problem that must be resolved. The measurement methodology in transmittance mode was already tested in some coloured glasses, including the comparison of the obtained results with a commercial spectrophotometer in order to validate the method employed with the IS system. However, a test of the analytical skills on a real sample was indispensable to understand the usefulness of the data acquired and possible advantages and disadvantages of such approach. The possibility to study stained glass windows from the *Cappella degli Scrovegni*, Scrovegni Chapel of Padua (Italy) had offered the necessary challenge for the IS device to demonstrate its potentialities in the field of the study of chromophores in glassy cultural heritage objects.

V.A Application of the IS system to the study of the chromophores of the glass *tesserae* of stained glass windows from the *Cappella degli Scrovegni di Padova*

The Scrovegni Chapel, dedicated to St. Mary of the Charity, frescoed between 1303 and 1305 by Giotto, upon the commission of Enrico degli Scrovegni, is one of the most important masterpieces of Western art. The building presents various windows in its construction. The correct maintenance of these glass structures is essential in order to prevent the integrity of the mural paintings. In fact, the stained glass windows are not of a high particular historical value if compared with the *opera* of Giotto. However, if they are damaged the consequences could be also harmful for the overwhelmed frescoes. For this reason, it has been decided to perform a restoration process to repair those glassy objects that presented several damages on its structure as structural deformations and several fractures of the vitreous *tesserae*. The intervention was an unique offer to test the IS methodology applied to the study of chromophores in glasses. In fact, the analysis with the IS device was not possible *in situ* in this case. In Figure V.1 an scheme of the building with the location of its glass surfaces and the nomenclature adopted is represented.

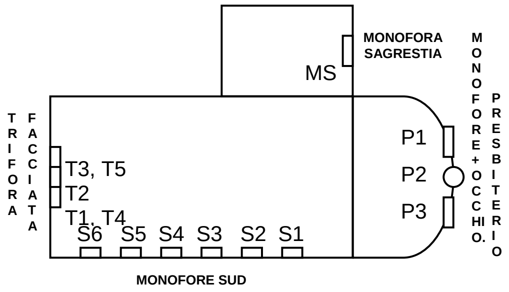


Figure V.1 – Scheme of the building with the location and nomenclature of its glass surfaces

The aims of the study were to study the stained glass windows in order to evaluate its conservation state, to identify the glass and to date a feasible period of production (it is believe that they have been created in the XIX century). In fact, it still is unknown the period of provenance of the stained glass windows present in the chapel and if they are all of the same period of execution, if they have been all produced with the same technology or if they have been some kind of substitution of some *tesserae* or panel. To reach these aims, the chemistry of cultural heritage work had planned a mainly non invasive approach through XRF and IS technique to collect as much information as possible of each stained glass window. Some samples had been additionally taken to perform some invasive analysis. In this dissertation, mainly IS data will be discussed. For practical reasons not all the stained glass windows could be remove at the same time and due to the importance of the building where they are placed the time at disposition to perform the analysis was really short. This has forced a large amount of research work because the knowledge of the objects was little and the purpose was to analyse as much as possible. This fact has highlighted another one of the benefits of the Imaging spectroscopy over the XRF spot technique. The IS device allows the record of huge amount of information in one acquisition. In fact, it has been notice during the study that in order to acquire as instance 2 panels of a stained glass window, IS analysis can be performed in one day, while XRF requires at least two or three days. Moreover, when the acquisition setup is ready IS allows to launch a measurement of a whole panel and continue with other activities during its acquisition whereas XRF need to be moved and refocused from *tesserae* to *tesserae* until complete the hundreds of glass pieces that form the panel. In fact the study of the chromophores could have been performed by other kind of instrumentation as FORS but it will have been time consuming. The aim was to demonstrate the usefulness and the analytical power of IS to solve such issues. The work is still in progress because there are several stained glass windows constituted normally by different panels. For this reason, only a part of the results will be presented that will be sufficient to demonstrate the validity of the analysis methodology through IS.

It is believe that this experiments are of interest because to the author knowledge, IS has not been used to the date to analyse stained glass windows.

V.A.1 ANALYSIS METHODOLOGY OF STAINED GLASS WINDOWS THROUGH IS

The general aspects regarding the acquisition setup in transmittance mode in the visible region using the IS device was already discussed in Chapter III. From the practical point of view, the analysis were performed in a dark laboratory of the Chemistry department. Taking in consideration the acquisition setup represented in Figure III.35, it was necessary to build a wood support in order to place each panel (the analysis were performed acquiring one panel per measurement) vertically in a secure way to avoid any harm of the samples and at the same time it must be able to contain the diffuser. In Figure V.2 it is possible to observe a panel of a stained glass window contained on the wood support and ready to be acquired by the IS device.

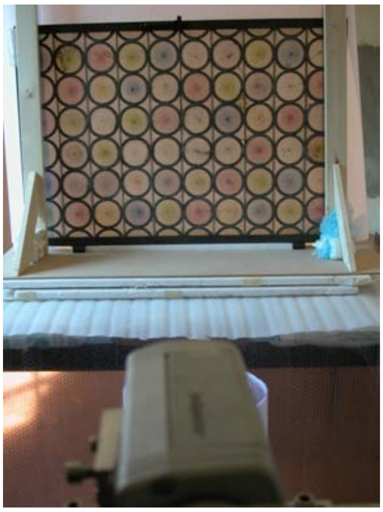


Figure V.2 – Stained glass window panel contained vertically on a specially built wood support

Thanks to this support the panels of the stained glass windows could be analysed by the IS device in transmittance mode. As it can be observed in Figure V.2, the panel is contained in it is iron frame. This structure gives mechanical stability to the system constituted by the glass *tesserae* and assembled with lead cames. During the removing operation of the first stained glass window placed at the church office, *sagrestia*, sample MS, an inconvenient forced the extraction of the superior panel from the window frame without its iron enclosing. For this reason this panel was extremely delicate and as a consequence it was impossible to performed the measurement in transmittance mode because it was not possible to put it vertically. This fact made necessary to perform the measurement employing another modality.

The modality adopted was nominated “double-transmission” because it was not found an adequate term in bibliography to describe the methodology. In this procedure the panels are positioned horizontally on a white scattering screen. The lamps and the IS device are placed on the same side of the sample under consideration and the panels are acquired in this geometry. The collected signal comes from the light of the lamps that has been transmitted through the glass, subsequently diffused back by the opaque white screen and finally transmitted again through the sample matrix. In this way, the second passage of the light coming from the scattering panel has been absorbed by the transparent object and it can be considered as a kind of “filtered” light. This procedure should enhance in this manner some weak spectral feature in comparison with the transmission mode. However, the results will permit to discuss if the solution executed is adequate or not. The standardized white panel employed in reflectance measurement has been used as a reference. Considering the measurement methodology, this panel is not the most suitable reference but it was the unique possible solution at disposition. The study with the IS system is aimed to identify the chromophores from a qualitative approach and the employment of this reference should furnish spectra sufficiently correct that must permit to reach this aim. The other aspects of the methodology were performed in a similar way as the measurement in reflectance mode (i.e. illumination system).

The signal collected with the “double-transmission” mode will be represented by the letter R, because the procedure was in many aspects similar to the reflectance mode but it must be reminded that R it is not the real diffuse reflectance. The intensity of the spectra that will be illustrated are represented as log(1/R) to be transformed to an unit that could be compared with the data obtained in transmittance that will be presented as absorbance, where A=log(1/T). In the following section, some of the results obtained in some panels of the stained glass windows of the

Scrovegni Chapel will be presented. They are a representation of the huge amount of data collected and of a work that still is in progress.

V.A.2 REPRESENTATIVE RESULTS

V.A.2.A MS stained glass window

The MS stained glass window is located in the church office and it is composed by two panels of approximately 73cm x 107cm. They are composed by slightly coloured circular glass tesserae, which are nominated venetian “rullo” and by colourless pieces of rhombus shape that will not be considered in the presentation of the results because its spectra in the range between 420nm and 850nm was not particularly characteristic. In Figure V.3 a scheme with the numeration and colour classification of the glass *tesserae* that constitutes the MS stained glass window and the (R, G, B) reconstruction obtained through the IS device.

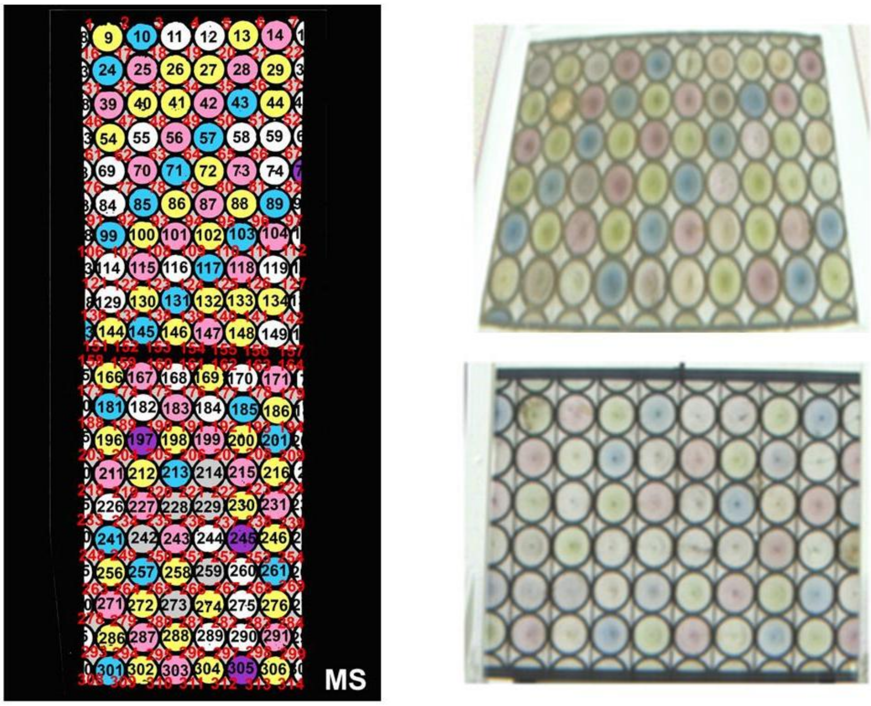


Figure V.3 – Schematic representation (left) of the MS stained glass window with the adopted numeration and colour classification of the glass *tesserae*, and (R, G, B) reconstructions (rotate of 90° respect to the orientation of the panels on the scheme) of the superior panel in “double-transmission” mode (right top) and of the inferior panel by transmittance mode (right bottom).

The *rullo* glass *tesserae* has been classified according to its colouration and the IS results will be commented divided by this criteria.

- <u>Blue *tesserae*</u>

In Figure V.4 the spectra of the blue glass *tesserae* obtained by imaging spectroscopy in “double-transmission” mode of the superior panel (left) and in transmission mode of the inferior panel (right) of the MS stained glass window are displayed.

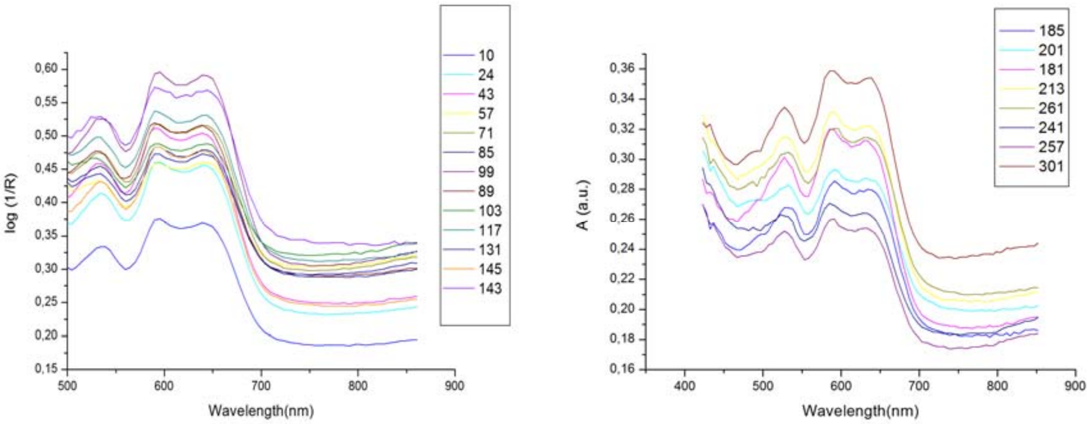


Figure V.4 – Visible spectra of the blue *tesserae* obtained by IS in “double-transmission” (left) and in transmittance (right) modes of the superior and inferior panels respectively of the MS stained glass window

It can be observed that the spectra obtained with both measurement modalities allow the clear identification of the blue chromophore, Co(II). In fact the band centred at 600nm corresponding to the transition $^4A_2 \rightarrow {}^4T_1(P)$ of d^7 Co(II) in a tetrahedral environment leading to spectral features at about 540nm, 590nm and 640nm that are evident from these spectra. It is known since ancient times that cobalt is a powerful colouring agent of glass that produces an intense blue colouration. It may be present as four-fold or six-fold coordinated, that produces a pale pink colour. However, glasses of this colouration with Co(II) are rare and has only been observed in low-alkali borate or phosphate glasses. The replacement of soda by potash in silicate glasses produces a more pure blue colouration that can be detected through the electronic spectra because it shifts of ~10nm the three maxima towards longer wavelengths [20, 38, 77, 88-91].

Co(II) has been identified different times thanks to IS as it has been showed in this doctoral dissertation. In fact, it has been demonstrate that electronic spectrum is a powerful tool to identified it. Moreover, during this analysis it has been noticed that the XRF spectra of the blue *tesserae* does not presented a clear signal of Co. This fact demonstrates in one more occasion the advantages and possibilities of a multi-technical approach. After the IS observations, the XRF spectra were reacquired optimizing the measurement conditions to detect this element and it was possible to observe a very weak peak. This is due to the fact than the *rullo* were not very coloured and a small amount of Co is able to produce this effect on the glass. The IS developed methodology, as UV-VIS-NIR reflectance/transmittance spectroscopy, has demonstrated its ability to reveal this chromophore.

Other aspect that is interesting of the spectra in Figure V.4, is that the “double-transmission” spectra have a signal to noise ratio better than the transmission ones. In fact, both acquisition modes obtain adequate results but the curves of the superior panel are clearly more defined. It is thought that this is due to the fact that the studied glass are fairly coloured and for this reason in transmission mode the signal is lower than in the alternative measurement modality. The double passage through the matrix of the sample enhance the absorbance.

Some of the *tesserae,* as the numbers 58, 119, or 259, that seem not coloured at naked eye and that had been represented as white/grey fragments in Figure V.4 contain Co(II) in its matrix because they display the characteristic features of this chromophore. The quantity was low because no blue colouration has been observed. However the IS information clearly indicates the presence of Co(II). It is possible that this fact was undesired and that the metal was some kind of impurity.

- <u>Pink, Purple, Violet *tesserae*</u>

There are many venetian *rullos* that present colouration from violet to pink and purple and they present in general very similar spectra that are illustrated in Figure V.5. In this case, the difference in terms of signal to noise ratio of the spectra with both modalities are less evident. In fact, they are rather similar from this point of view. The obtained IS spectra are characteristic of the Mn(III) chromophore. Manganese could be present as Mn(II) or Mn(III) but is the latter form which produces the purple colouration. Its typical spectrum shows a broad asymmetric band centred at ~480nm and a shoulder at ~660nm produced by the d^4 Mn(III) surrounded by six oxygen atoms. The IS spectra clearly display these features allowing its identification.

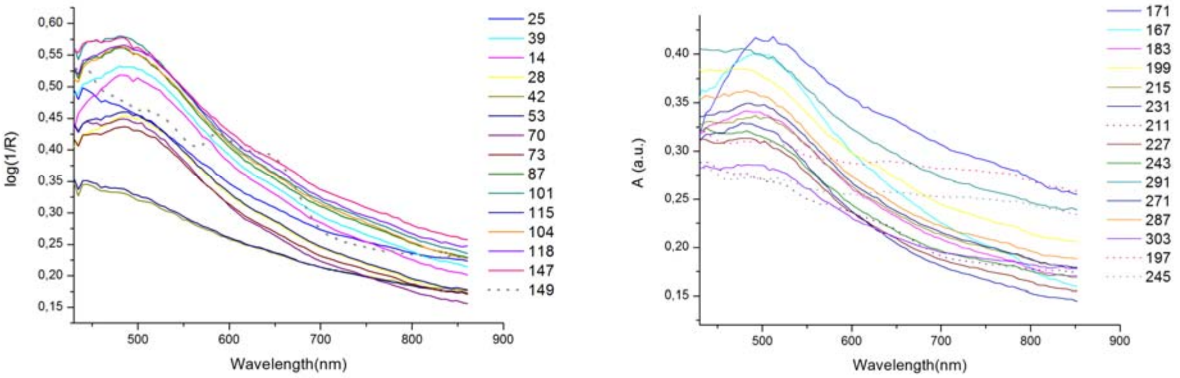


Figure V.5 – Visible spectra of the pink-purple-violet *tesserae* obtained by IS in "double-transmission" (left) and in transmittance (right) modes of the superior and inferior panels respectively of the MS stained glass window

The Mn (II) also presents a visible spectra with an asymmetric band but centred at 430nm but it is very weak (100 times less or more than the one of Mn (III) because it is spin forbidden).The colour of manganese glass will be determined by the ratio between the colouring Mn(III) and the non coloured Mn(II) form. The use of this chromophore in glasses dates back to the 1400 (b.c.) and sometimes it could be an impurity of the raw materials. It is considered that amounts higher than the 1% are intentioned. In Figure V.5 it is possible to observe that some *tesserae* have a pointed spectral curves that in addition to the spectral features of the Mn(III) they present to the ones of Co(II) [20, 38, 77, 88-91, 145, 146].

- Yellow-Green *tesserae*

In Figure V.7 the spectra of the yellow-green glass *tesserae* obtained by imaging spectroscopy in "double-transmission" mode of the superior panel (left) and in transmission mode of the inferior panel (right) of the MS stained glass window are displayed.

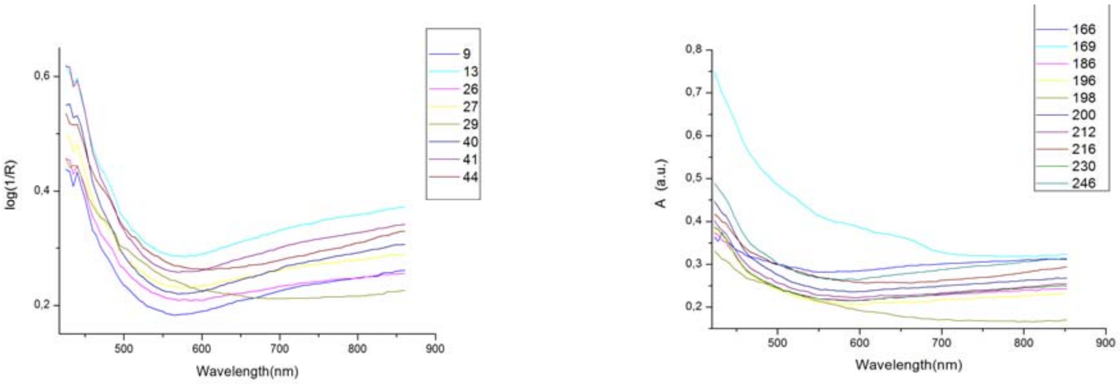


Figure V.7 – Visible spectra of the yellow-green *tesserae* obtained by IS in "double-transmission" (left) and in transmittance (right) modes of the superior and inferior panels respectively of the MS stained glass window

The IS spectra show an intense band in the shorter wavelengths with a weak feature at nearly 436nm. Unfortunately, in this case the obtained data do not allow the clear identification of the chromophore. However, from the available information it can be hypothesized that the yellow-green hue is provoked by iron. In order to verify this supposition a wider wavelength interval would be required to observe another features towards the UV and the NIR. The colouration of glass by iron is one of the most important. As an impurity, it produces a slight green colouration and as a desired chromophore it generates green-grey-brownish hues. Usually, it is present as Fe(II) that has a band at 1050nm or Fe (III) that is characterized by features at 380nm, 420nm and 435nm [20, 38, 77, 88-91, 145, 146].

None of the chromophores identified by IS are able to date the *tesserae* glass of the MS stained glass window. However, the results demonstrate the ability of the developed device to simultaneously record a large number of spectra of these coloured vitreous that allow the characterisation of the glass chromophores.

V.A.2.B P1 stained glass window

In this case only few interesting results will be commented. In fact, it must be taken into account that the P1 stained glass window, which is located at the sanctuary, *presbiterio*, of the chapel, is a very wide stained glass window formed by four panels constituted by hundreds of glass *tesserae*. They can be divided in two typologies: venetian *rullo* that are slightly coloured and triangular "star" tesserae which are strongly coloured. It is beyond the purpose of this doctoral dissertation to discuss thoroughly the totality of the data. Moreover, the global study of most of the vitreous surfaces of the chapel by IS still is a work in progress. For these reasons, in this section the spectra obtained by IS that have allowed the identification of another chromophores will be briefly presented and commented. As for the MS window, the IS spectra has confirmed the presence of the chromophores Co(II) and Mn(III) and the feasible hypothesis of the occurrence of iron, in numerous glass tesserae. In addition to the study of the chromophores of the glass tesserae, the results obtained by the IS device in transmittance and in "double-transmission" modes will be compared. In fact, two panels of the P1 window have been acquired in both modalities with this purpose. The results of the MS window previously commented have shown that both approach furnish sufficiently adequate results that permit the study of glass chromophores. In this case, the information given by both methodologies will be compared in order to evaluate which is more adequate for what kind of sample. In Figure V.8, a picture of one of the panels of the P1 window is reported.

Figure V.8 –Panel of the stained glass window P1

For various red "stars", the collected IS spectra show a characteristic peak at 560nm due to the presence of colloidal copper which has been use to produce red hues it is known since ancient times. In this vitreous pieces, the element copper has been used also to produce blue-turquoise-green colourations of numerous glass tesserae, venetian "rulli" and triangular "stars". To create such effect, the element is present as Cu(II) and its spectrum is characterized by a broad and asymmetric band from 700-900nm. Numerous spectra acquired thanks to the IS device display this typical feature, confirming the use of Cu(II) as chromophore in the production of this object. The employment of Cu(II) to produce such colours was also known since antiquity times. In Figure V.9 the spectra of triangular *tesserae* with the characteristic peak of colloidal copper and the asymmetric broad band of Cu(II) are represented [20, 38, 77, 88-91, 145-147].

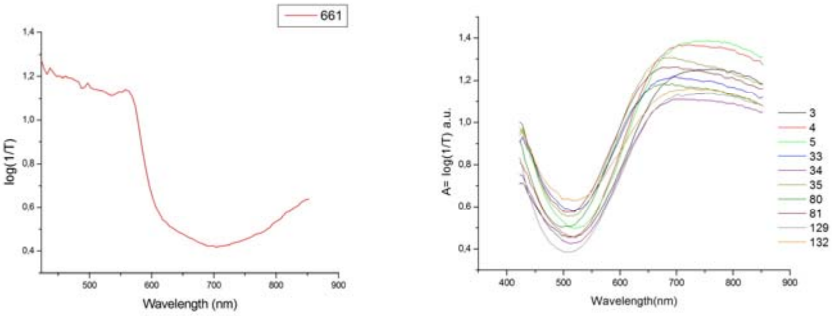


Figure V.9 – Visible spectra of a red (left) and several turquoise "stars" *tesserae* obtained by IS in transmittance mode of the P1 stained glass window

One of the greenish "rullo" presents an interesting spectrum, which is displayed in Figure V.10.

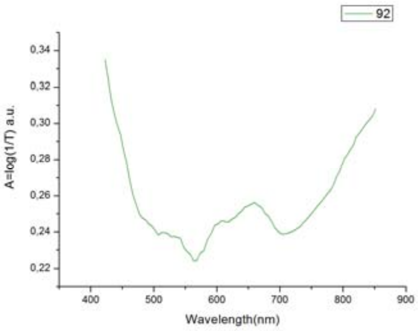


Figure V.10 – Visible spectrum of a green “rullo” *tessera* of the P1 window obtained by IS in transmittance mode

This spectrum has the characteristic features of the glass chromophore Cr(III). The typical green colour produced by this metal is caused by a triple absorption band at around 630, 650 and 675 nm respectively and another slight one at around 435nm. The spectrum obtained also suggest the presence of Co(II) in this greenish *tessera* which features are not so evident as in the case already commented for the MS window but that still are evident as it can be observed by the band present on the spectrum at ~540nm. Chromium has been employed to produce Cr(III) emerald green and Cr(VI) yellow in glass since the XIX century[24, 38, 77, 88-91, 145-147]. It is the unique chromophore of the ones detected that could be used to “date” the stained glass windows, even so being found only in a glass tesserae it could be also a substitution of a single piece. In this case, XRF spectra did not show the signal of neither the Cr nor the Co. One more time the IS technique has showed its sensibility to detect some chromophores and its utility in one combined approach with XRF as instance. In Figure V.11 a detail of the XRF spectrum of this glass tesserae is illustrated.

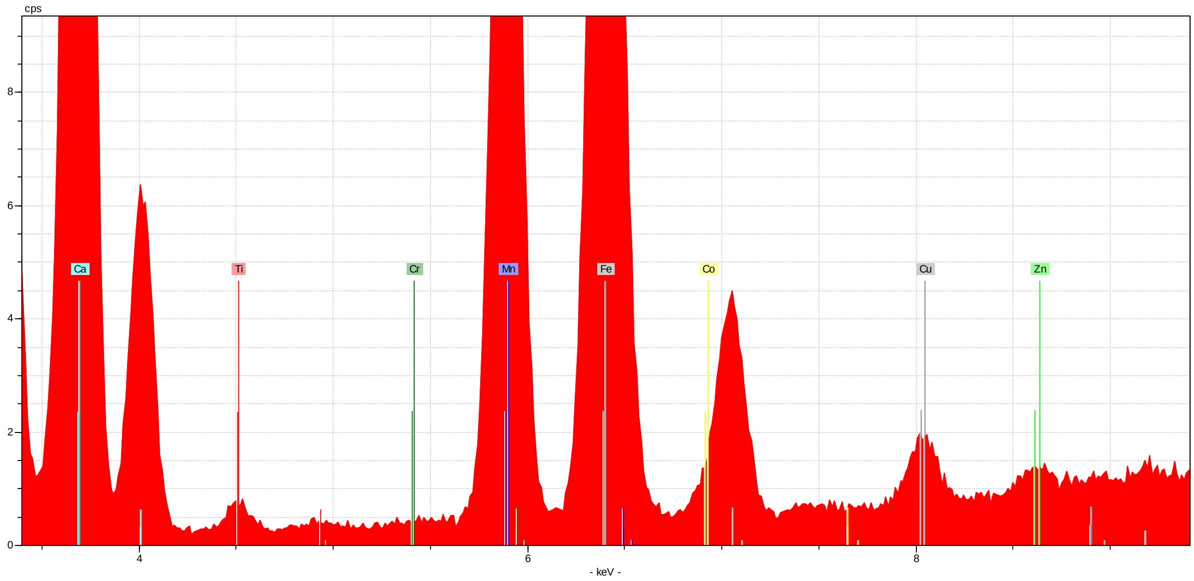


Figure V.11 – Detail of the XRF spectra of the greenish “rullo” *tessera* of the P1 window

The results obtained through the IS device in transmittance and in “double-transmission” modes are generally speaking adequate and for many glass *tesserae* comparable in terms of “quality” of the spectra. However, in several cases it has been observed that transmittance mode is more adequate for samples with intense colouration (“stars”) whereas the “double-transmission” furnish better results for some vitreous samples that present slight colourations (“rulli”). In Figure V.12 the spectra obtained on a same “rullo” *tesserae* by both modalities is showed.

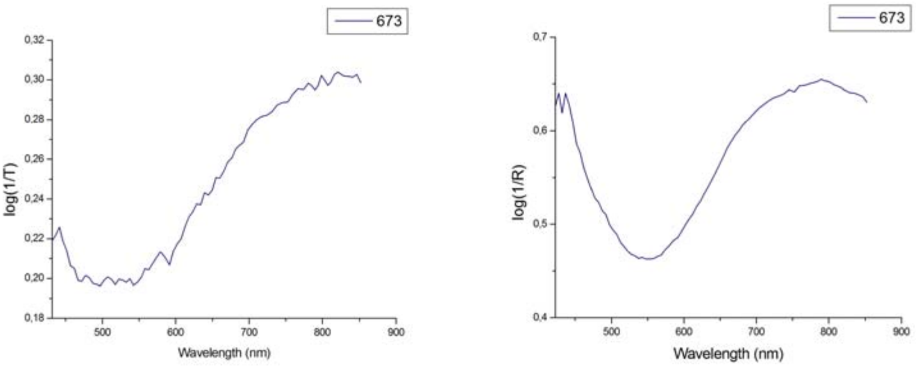


Figure V.12 –Spectra of a “rullo” *tessera* obtained in transmittance (left) and “double-transmission” (right) modes

It can be noticed that for this sample which present a weak blue colouration the spectra obtained in transmittance is more noisy than the one collected in “double-transmission”mode. It has been already said that this is thought to be produced by the enhancement in this modality of the features. However both spectra allow the identification of the chromophore, Cu(II) due to the visible broad band centred at ~800nm. On the other hand, if the sample under consideration present a strong colouration, as for the triangular tesserae, the transmittance mode seems more adequate as it is illustrated in Figure V.13.

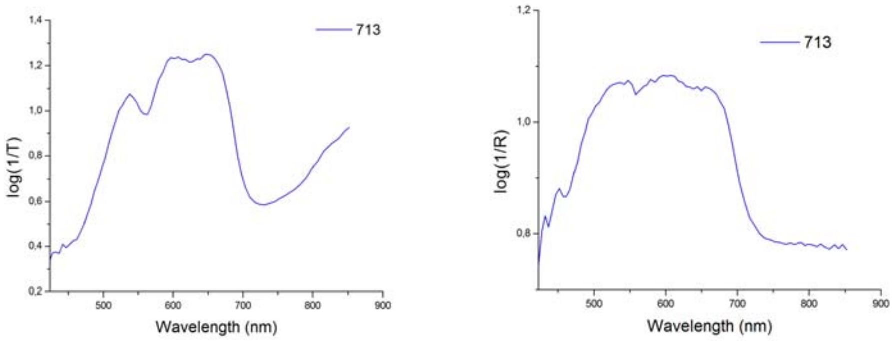


Figure V.13 –Spectra of a “star” *tessera* obtained in transmittance (left) and “double-transmission” (right) modes

Both measurement modalities as it is showed in Figure V.13 allow the identification of the chromophore Co(II) but the spectrum in transmittance is clearly more defined. It is possible that in this condition with the alternative “double-transmission” mode the intense colouration saturates the band. However, in general the data collected by both modalities are adequate and they have demonstrated its capacity in the identification of glass chromophores.

V.A.2 CONCLUSIONS

The presented results has demonstrated the potentialities of the IS technique to simultaneously collect numerous visible spectra that allow the characterisation of the glass chromophores. It could represented an interesting alternative to spot techniques that when dealing with such vast objects are time consuming.

The IS device has identified Co(II), Mn(III), Cu(II), Cr(III) and colloidal copper used to colour glass. From the IS spectra, it has been hypothesized the feasible use of Fe(III) in some yellow-green *tesserae* but a wider wavelength interval would allow clearest conclusion in this particular case of glass fragments. The chromophores identified have been used since ancient times with the unique exception of Cr(III) that was in use since the XIX century. However, due to the identification of the element in only one glass *tesserae* that could have been replaced it is not possible to made a certain conclusion of the elaboration period of the samples. Anyway, the technique has given valuable information about the production technique of these stained glass window.

In addition to the transmittance mode that was previously developed as it has been already commented in Chapter III, a “double-transmission” mode was adopted due to the impossibility in some delicate cases to apply the former modality. Both furnish adequate qualitative results that permit to characterize glass chromophores. However, from the experimental results it seems that the “double-transmission” spectra have a better signal to noise ratio for weak coloured sample whereas the transmittance ones are more defined for glass pieces that present strong colouration.

The application of IS technique to study vitreous objects could be an interesting approach to this kind of analytical problems. Moreover, the results discussed have shown that the multi-technical approach consisting in IS and XRF can be remarkable. In fact, the data reveal that both methods can be integrated and that the IS information is useful in some situations as for the identification of Co(II) and Cr(III). In addition the possibility to simultaneously acquired hundreds of samples is a strong advantage of this technique.

As it has been said before, this is an innovative application of the IS technique. The data that had been acquired could be post processed in order to obtain a more visible representation of the data. However, as it has been already mentioned, this still is a work in progress but the results are really encouraging.

Conclusions

This research work has dealt with the application of an imaging spectroscopy device to face analytical problems regarding the chemistry for cultural heritage field. The system was designed and built by the LUXOR laboratory and by the DEI department of the university of Padua. In fact, the whole project has been developed in a close collaboration of those structures with the chemistry for cultural heritage group of the chemistry department of the university of Padua due to the fundamental necessity of both chemical and engineering competences.

The technique is gaining importance in the particular field for the study of works of art due to its possibilities to collect large amount of information in a non invasive way and *in situ*. However, it still presents challenges and aspects that must be considered. This research work has discussed some of these issues. The first chapters of this doctoral dissertation has presented theoretical aspects regarding the state of the art of the technique and of the particular materials that constitutes some objects of the cultural heritage area that are of great importance in order to correctly focus the successive chapters that deal with different practical aspects.

The central part of the research work has dealt with the development of a measurement methodology to obtain reflectance spectra with the IS device. Despite the discouraging results obtained during the first tests, different improvements on the illumination system, on the acquisition procedure, and on the processing of the acquired data had lead to adequate results. Different tests performed on *ad hoc* samples had demonstrated that the developed methodology gives spectrum in the range between 420nm and 850nm with an average spectral resolution of 5.2nm that are in good correspondence with the data obtained by a spectrophotomer and with the information found on the references. Experiments that had included artificial ageing of *ad hoc* samples has demonstrated that the system could represent an interesting analytical tool that allows the characterisation, differentiation, mapping and monitor of simple paint film models. The results strongly suggest that the developed IS methodology to collect reflectance spectra could be applied to solve different analytical problems regarding artworks issues and that the device could be an important component of a non invasive mobile laboratory. There are some aspects under discussion that could be improved, as a more accurate calibration through the use of internal standards that can be included in the field of view of the instrument. However, the results exposed in Chapter III clearly show the difference between the spectra of the first tests and those obtained on the specially prepared and aged samples. The first ones where totally disappointing whereas the latter are encouraging and demonstrated the potentialities of such type of systems on the non invasive study of cultural heritage objects.

Even though the system was built to acquired spectra in reflectance, the system is versatile and has been adapted to perform measurements in transmittance mode in order to study wide objects as stained glass windows. These part of the research work was particularly challenging due to the innovation that suppose the study of this kind of object with this technique in this modality.

The developed system has been successfully apply to the study *in situ* of a real mural painting. The IS technique was integrated with XRF and the approach was of extreme utility to accomplish the objectives of an interdisciplinary study of the artwork that had actively assisted a restoration process that was executed to recover the mural painting. The IS system has been able to collect large amount of data that had allowed the identification of most part of the pigments of the artists palette. The spectra collected were adequate, specially taking into consideration the difficult *in situ* conditions. The developed measurement methodology could be applied to study the artwork giving good results and demonstrating his versatility. In addition, IS has also assisted some restoration phases thanks to virtual restoration and could represent an interesting interface to base a digital data management of the artworks.

Finally, the developed system has been applied to study in transmittance mode the chromophores of the glass *tesserae* of some of the stained glass windows of the Scrovegni chapel of Padua. The results show the potentialities of the IS system to study the colouring agents of the vitreous objects. Due to a problem occurred during the removing operation of one of the panels studied, the analysis in transmittance were not a feasible option. In one more occasion, the built IS system has proved its ability to adapt to different problematic situations that could happen when analysing objects regarding the cultural heritage field because the complications were overcome employing an alternative “double-transmission” mode. Moreover, the obtained results allowed to prove that the developed transmission methodology for intense coloured glass objects is adequate but that “double-transmission” IS spectra are generally better in terms of signal to noise ratio when dealing with glasses weak coloured.

The different results highlight the different solutions that IS can bring to the chemistry for the cultural heritage and its possible integration to non invasive and transportable laboratories. The work still is in progress but the present research work illustrates the multiple tasks that IS can perform and the different analytical problems that it could help to solve if used correctly. There still are aspects that must be revised, tested and examined. One of those that represent a future prospective of the research work is the re-elaboration of the hyperspectral data cube in order to obtain more meaningful results, as instance visual representations of the information collected that would summarize part of the data collected in an image . Another aspect that can be improved is the wavelength interval of work. Obviously a wider range would increase the number and type of materials that could be identified by means of the IS system. However, this necessarily implies changes in the basic components of the instrumentation.

In fact one of the limitations of the IS system is its narrow wavelength range were the system is reliable and the lower fingerprinting capacity specially if compared with IR spectroscopy for example. However, as it has been previously commented, when dealing with analytical problems regarding cultural heritage objects the multi-technical approach is a good alternative in order to integrate the information given by various techniques. During this research work, IS has been integrated with XRF giving good results in the identification of inorganic materials, as the pigments of the mural painting of S. Caterina. The characterization of organic materials would require the integration with other techniques more adequate as IR or Raman, because XRF is not sensible to these compounds.

As a general conclusion, it could be affirmed that the imaging spectroscopy technique presents characteristics and potentialities that make it very suitable to deal with analytical problems of the cultural heritage field. The present doctoral dissertation had demonstrated this by different results obtained on different kind of samples. The research work gives solutions to developed measurement methodologies and also to interpret the recorded data that contribute to reach non invasive methods that could be more adequate to deal with the issues regarding the chemistry for cultural heritage field.

Annexes

Annex I: Other instrumental techniques

This doctoral dissertation deals with Imaging Spectroscopy. However other techniques had been employed to develop the research work. In this annex, the main technical details of the other instruments employed are briefly described.

AI.1 UV-VIS-NIR Spectroscopy

AI.1.1 FIBRE OPTICS REFLECTANCE SPECTROSCOPY

The analysis with this technique were performed by the Mobile laboratory MOLAB research group of the *Università degli studi di Perugia* (Italy). They have used a portable spectrophotometer where the excitation source is a deuterium halogen lamp coupled to a bifurcated bundle of quartz fibres that collect and transfer the reflectance signal to a high sensitivity Avantes CCD detector (200-1100 nm, spectral resolution 2 nm). The probe-head is usually positioned at 45° to reduce the specular component. Calibration is performed by means of 99% Spectralon diffuse reflectance standard.

AI.1.2 UV-VIS-NIR BENCHTOP SPECTROPHOTOMETERS

During this research work numerous UV-VIS-NIR spectroscopy measurements were performed by two commercial laboratory spectrophotometers, a Cary 5 and a Cary 5000. Both were used to acquired diffuse reflectance spectra whereas to study samples in transmittance mode only the first instrumentation was employed.

The double-beam Cary 5 spectrophotometer (Varian Inc., Palo Alto, CA) was employed to obtain UV-VIS-NIR spectra in transmittance and reflectance mode. The instrumentation is equipped with an integrating sphere coated with polytetrafluoroethilene (PTFE). The geometry used excluded the specular component of the reflected light. The spectra were collected within a range from 300nm to 2500 with a spectral resolution of 1nm.

In addition, a Cary 5000 UV–Vis–IR spectrophotometer (Varian Inc., Palo Alto, CA) equipped with an integrating sphere accommodating a PMT/PbS detector was also used. Reflectance values were acquired at 1.0nm intervals over the 300–2500 nm range.

AI.2 Optical Microscopy (OM)

Samples have been observed using an Axiotech 100 Zeiss optical microscope. All photos have been taken using a digital camera Nikon Coolpix 5000 and a Nikon D90 interfaced with the optical microscope.

The microscope has the following magnifications: 5X, 10X, 20X, 50X and 100X. It works in three main configurations: brightfield (standard configuration), darkfield (the light pathway in this configuration in changed, it helps particularly for the vision of the colours of the plane glass) and DIC (differential interference contrast, that increases the contrast at the surface of the samples). Polarised light is also available.

AI.3 Light exposure and weathering chamber

The artificial accelerated ageing programs where performed on a light exposure and weathering chamber Atlas Suntest CPS+ (Heraus, Germany), equipped with a Xenon-lamp and a special UV glass filter in order to emulate an outdoor solar exposure in the range from 295nm to 800nm.

AI.4 X-Ray Photoelectron Spectroscopy (XPS)

Some of the materials employed in this research work has been characterized through XPS spectroscopy using a polymer-based adhesive tape to fix the powder or directly piece of the sample. Spectra have been taken by an X-Ray Photoelectron spectrometer PERKIN ELMER Φ5600ci equipped with a double anode X-Ray Source (Mg/Al) and a monochromatic Al X-Ray source. The anodes work at 20 mA and 14 kV conditions, emitting AlKα (1486.6 eV) and MgKα (1253.6 eV) rays. A Concentric Hemispherical Analyser has been used to collect the output electrons. Analysed areas are circles of 0.8 mm in diameter. The scan range is 0 – 1350 eV (AlKα source) or 0 – 1150 eV (MgKα source) according to the source adopted. A charge neutraliser has been used to avoid spectral shift in insulating samples and all spectra have been corrected according to charging effect, assigning a binding energy of 284.8 eV to the C1s peak due to surface hydrocarbon contamination.

AI.5 X-Ray Fluorescence (XRF)

A portable XRF system, Artax μXRF spectrometer, from Bruker AXS was employed to collect XRF spectra. It consists of a 50-kV Mo excitation tube, a Peltier-cooled silicon drift detector with an energy resolution of 150eV at 5.9KeV and 10 x10^3 cps. It allows the detection of elements from Al to U and, with optional He purging, elements down to Na can be detected.

AI.6 Fourier Transform Infrared Spectroscopy (FT-IR)

Some samples were analysed by means of FT-IR spectroscopy on KBr pellets using a Nicolet Nexus FT-IR spectrophotometer with a pyroelectric deuterated triglycine sulphate DTGS KBr detector in the wavelength range from 4000 to 400 cm^{-1} with an spectral resolution of 2 cm^{-1}.

Annex II: Synthesized pigments

Some of the compounds employed in the preparation of different samples regarding this doctoral dissertation were synthesized in laboratory. In particular, various copper based pigments namely verdigris, copper resinate, green verditer (artificial malachite) and blue verditer (artificial azurite). The synthesis were performed following the indications founded on different references [73-76, 81, 99, 102, 110, 112, 116, 148]. Some details of these operations will be briefly commented. The products which colours correspond well to the expected results were characterized by OM, XPS and IR.

AII.1 Verdigris

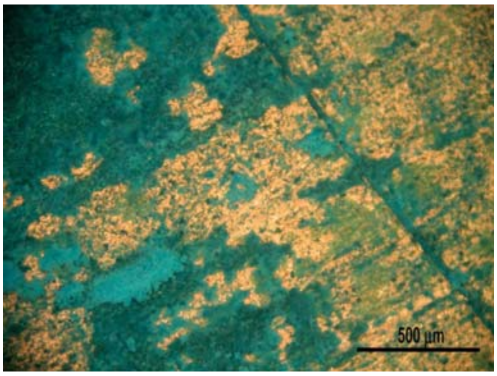
Verdigris is a blue-green Cu(II) carboxylate complex at different hydration degrees which was produced basically from the reactions of metallic copper in the presence of acetic acid since ancient times. The term verdigris refers to various Cu(II) acetate compounds that can be divided into two groups, basic and neutral verdigris. The latter is also called *verde eterno* and its chemical formula is $Cu(CH_3COO)_2 \cdot H_2O$. The former is the product that was synthesized on laboratory.

Basic verdigris can contain the following copper acetates alone or in determined mixture:

1/ $[Cu(CH_3COO)_2]_2 \cdot Cu(OH)_2 \cdot 5H_2O$	(2:1)	Blue
2/ $Cu(CH_3COO)_2 \cdot Cu(OH)_2 \cdot 5H_2O$	(1:1)	Blue
3/ $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_2$	(1:2)	Blue
4/ $Cu(CH_3COO)_2 \cdot [Cu(OH)_2]_3 \cdot 2H_2O$	(1:3)	Green

In the laboratory, it was synthesized following two methods: the *synthetic* and the *ancient.* The first approach employs chemical reagents to obtain the verdigris in different steps. Firstly, $CuSO_4 \cdot 3Cu(OH)_2$ is prepared from $CuSO_4 \cdot 5H_2O$ and NH_4OH. Then, the obtained product is converted to $Cu(OH)_2$ with NaOH. Finally, CH_3COOH is added to the hydroxide forming a mixture that must dry. The green-blue pigment is obtained after washing and grinding the powder.

The ancient method simply consists on the exposure of a metallic copper sheet that was previously dampened with a concentrated NaOH or KOH solution to the vapours of acetic acid in a container for two weeks. The pigment is formed on the metallic surface and it is necessary to scrape off to obtain the powder. In Figure AII.1 an OM picture of one of the prepared copper sheets is showed partially covered by the verdigris.



FigureAII.1-Synthesized verdigris over the copper sheet surface

AII.2 Copper resinate

Copper resinate was frequently used from the XV century and it is a transparent green glaze obtained by mixing copper pigments, usually verdigis, with terpenic resins. It is a complex mixture of copper carboxylate complexes of resin and fatty acids that could be used fresh or as a dry powder that was normally dispersed in a drying oil or *tempera grassa* medium.

The pigment was obtained by adding finely grinded verdigris to turpentine heated to 80°C. The quantity depends on the desired hue. Turpentine spirit was incorporated at room temperature in order to correct the fluidity of the mixture. The amorphous brilliant green layer was then spread on a surface where the product dries. The powder of the pigment was obtained by grinding the cold and desiccate layer.

AII.3 Blue and Green Verditer

Blue and Green verditer are the synthetic products with the same chemical formula of the mineral used since antiquity as pigments azurite $Cu_3(CO_3)_2(OH)_2$ and malachite $Cu_2CO_3(OH)_2$.

Synthetic copper carbonate hydroxide blues and greens develop a spherulitic habit that is distinctly different from the crushed crystal shards associated with azurite and malachite when viewed microscopically. Blue and Green verditer are paler than natural azurite and malachite, but otherwise its stability and other properties are identical.

The synthesis of these compounds is very simple. They are obtained by the slow addition of a $CuSO_4 \cdot 5H_2O$ solution to a Na_2CO_3 solution. In the case of blue verditer the reaction take place using an ice bath, whereas the green verditer is obtained in an water bath at 40°-50° C. The powders are filtered, then dried and grinded. The only precaution that must be taken in the case of blue verditer is to do not leave it long times in water because it is instable and the product can be transformed to green verditer:

$$Cu_3(CO_3)_2(OH)_2 + H_2O \quad \leftrightarrow \quad Cu_2CO_3(OH)_2 + CO_2$$

In fact, in some synthesis the initial blue verditer pigment has suffered the transformation to green verditer.

References

[1] E. Ciliberto, G. Spoto (Eds.), *Modern Analytical Methods in Art and Archaeology*, Chemical Analysis, Wiley, New York, A Series of Monographs on Analytical Chemistry and its Applications, vol. 155, 2000, J.D. Winefordner (Ed).

[2] Proceedings of the International Workshop SMW08. In Situ Monitoring of Monumental Surfaces. "7-29 October 2008, Florence, Edited by P.Tiano and C.Pardini, Florence, Edifir.

[3] K. Martinez, J. Cupitt, D. Saunders, R. Pillay, "Ten Years of Art Imaging", Proceedings of the IEEE, Vol. 90, No. 1, JAN 2002, pp. 28-41.

[4] A. Pelagotti,A. Del Mastio, A. De Rosa, A. Piva, "Multispectral imaging of paintings", IEEE Signal Processing magazine, Vol. 25, No. 4, JUL 2008, pp. 27-36.

[5] J. R. Mansfield, M. G. Sowa, C. Majzels, C. Collins, E. Cloutis, H. H.Mantsch, "Near infrared spectroscopic reflectance imaging: supervised vs. unsupervised analysis using an art conservation application", Vibrational Spectroscopy, Vol. 19, No. 1, FEB 1999, pp. 33-45.

[6] J. P. Mohen, M. Menu, and B. Mottin, "Mona Lisa: Inside the Painting", Harry N. Abrams, New York, NY, USA, 2006.

[7] M. Barni, A. Pelagotti, A. Piva, "Image processing for the analysis and conservation of paintings: Opportunities and challenges", IEEE Signal proceesing magazine, Vol. 22, No. 5, SEP 2005, pp. 141-144.

[8] N. Brusco, S. Capeleto, M. Fedel, A. Paviotti, L. Poletto, G. M. Cortelazzo, G. Tondello, "A system for 3D modeling frescoed historical buildings with multispectral texture information", Machine Vision and Applications, Vol. 17, No. 6, DEC. 2006, pp. 373-393.

[9] A.Paviotti, F. Ratti, L. Poletto, G. M. Cortelazzo, "Multispectral Acquisition of Large-Sized Pictorial Surfaces," EURASIP Journal on Image and Video Processing, Vol. 2009, Article ID 793756, 17 pages, 2009. doi:10.1155/2009/793756.

[10] C. Bisulca, M. Picollo, M. Bacci, D. Kunzelman, “UV-Vis-Nir Reflectance Spectroscopy of Red Lakes in Paintings” in 9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008.

[11] C. Miliani, A. Romani, G. Favaro , “A spectrophotometric and fluorimetric study of some anthraquinoid and indigoid colorants used in artistic paintings”, Spectrochimica Acta Part A, Vol. 54, No. 4, APR 1998, pp. 581-588.

[12] S.P. Best, R.J.H. Clark, M.A.M. Daniels, C.A. Porter, R. Withnall, “Identfication by Raman Microscopy and Reflectance Spectroscopy of Pigments on an Icelandic Manuscript”, Studies in Conservation*,* Vol. 40, No. 1, pp. 31-40, FEB 1995.

[13] P. Vandenabeele, R. Garcia-Moreno, F. Mathis, K. Leterme, E. Van Elslande,F.P. Hocquet, S. Rakkaa, D. Laboury, L. Moens, D. Strivay,M. Hartwig, “Multi-disciplinary investigation of the tomb of Menna (TT69), Theban Necropolis, Egypt”, Spectrochimica Acta Part A, Vol. 73, No. 3, Sp. Iss. SI , AUG 2009 pp. 546-552.

[14] M.Picollo, M. Bacci, L. Boselli, C. Cucci, A. Casini, F. Lotti, M. Poggesi, B. Radicati, L. Stefani “Non-invasive spectroscopic techniques for the diagnosis and conservation of historic surfaces and wall paintings”, Proceedings of the International Workshop SMW08. In Situ Monitoring of Monumental Surfaces. “7-29 October 2008, Florence, Edited by P.Tiano and C.Pardini, Florence, Edifir, pp. 31-36.

[15] L. Appolonia, D. Vaudan, V. Chatel, M. Aceto, P.Mirti. “ Combined use of FORS, XRF and Raman spectroscopy in the study of mural paintings in the Aosta Valley(Italy)”, Analytical and bioanalytical chemistry , Vol. 395, No. 7, DEC. 2009 pp. 2005-2013.

[16] M.Leona, J. Winter, “Fiber Optics Reflectance Spectroscopy: A unique tool for the investigation of Japanese paintings”, Studies in conservation, Vol. 46, No. 3, 2001, pp. 153-162.

[17] M. Bacci, D. Magrini, M. Picollo, M.Vervat, “A study of the blue colors used by Telemaco Signorini (1835-1901)”, Journal of Cultural Heritage, Vol. 10, No. 2, APR-JUN 2009 , pp.275-280.

[18] G. Dupuis, M. Menu, “Quantitative characterisation pigment mixtures used in art by fibre-optics diffuse-reflectance spectroscopy”, Applied Physics A- Materials Science & Processing, Vol. 83, No. 4, JUN 2006, pp.469-474.

[19] P.Mirti, A.Lepora, L. Saguì, “Scientific analysis of seventh-century glass fragments from the crypta Baldi in Rome”, Archaeometry, Vol. 42, part 2, AUG 2000, pp. 359-374.

[20] M. Bacci, A. Corallini, A. Orlando, M. Picollo, B. Radicati, “The ancient stained windows by Nicolo di Pietro Gerini in Florence. A novel diagnostic tool for non-invasive in situ diagnosis“, Journal of Cultural Heritage, Vol. 8, No. 3, JUL-SEP 2007, pp.235-241.

[21] C. Balas, V. Papadakis, N, Papadakis, A. Papadakis, E. Vazgiouraki, G. Themelis “A novel hyper-spectral imaging apparatus for the non-destructive analysis of objects of artistic and historic value”, Journal of Cultural Heritage, Vol. 4, Supplement 1, JAN 2003, pp. 330s-337s.

[22] A. Casini, F. Lotti, M. Picollo, L. Stefani, E. Buzzegoli, “Image spectroscopy mapping technique for non-invasive analysis of paintings “, Studies in conservation, Vol. 44, No. 1, 1999, pp. 39-48.

[23] J.K. Delaney, J.G. Zeibel, M. Thoury, R. Littleton, M. Palmer, K. M. Morales, E.R. de la Rie, A. Hoenigswald, “Visible and Infrared Imaging Spectroscopy of Picasso's *Harlequin Musician*: Mapping and Identification of Artist Materials *in situ*” Applied Spectroscopy, Vol. 64, No. 6, JUN 2010, pp.584-594.

[24] M. García-Heras, N. Carmona, C. Gil, M. A. Villegas, “Neorenaissance/Neobaroque stained glass windows from Madrid: a characterisation study on some panels signed by the *Maumejean Frères* company”, Journal of Cultural Heritage, Vol. 6, No. 2, APR-JUN 2005, pp. 91-98.

[25] M. Kubik, “Chapter 5 Hyperspectral Imaging: A New Technique for the Non-Invasive Study of Artworks” in Physical Techniques in the Study of Art, Archaeology and Cultural Heritage Edited by D. Creagh, D. Bradley, Vol. 2, 2007, Elsevier, Amsterdam, pp. 199-259.

[26] R. N. Clark, *Spectroscopy of Rocks and Minerals, and Principles of Spectroscopy*, http://speclab.cr.usgs.gov/PAPERS.refl-mrs/refl4.html

[27] P. Geladi, H. F. Grahn, “Multivariate and Hyperspectral Image Analysis”, in: R. A. Meyers (Ed.), *Encyclopedia of Analytical Chemistry*, John Wiley & Sons Ltd, 2008, pp. 14349-14374.

[28] M. Bacci, A. Casini, C. Cucci, A. Muzzi, S. Porcinai, “A study on a set of drawings by Parmigianino: integration of art-historical analysis with imaging spectroscopy”, Journal of Cultural Heritage, Vol. 6, No. 4, DEC 2005, pp. 329-336.

[29] J.R. Mansfield, M. Attas, C. Majzels, E. Cloutis, Collins C, H.H. Mantsch, “Near infrared spectroscopic reflectance imaging: a new tool in art conservation”, Vibrational Spectroscopy, Vol. 28, No. 1, FEB 2002, pp. 59-66

[30] K. Melessanaki, V. Papadakis, C. Balas, D. Anglos, “Laser induced breakdown spectroscopy and hyper-spectral imaging analysis of pigments on an illuminated manuscript”, Spectrochimica Acta Part B, Vol. 56, No. 12, DEC 2001, pp. 2337-2346.

[31] G. Payne, C. Wallace, B. Reedy, C. Lennard, R. Schuler, D. Exline, C. Roux, “Visible and near-infrared chemical imaging methods for the analysis of selected forensic samples”, Talanta, Vol. 67, No. 2, AUG 2005, pp. 334-344.

[32] P. Geladi, J. Burger, T. Lestander, “Hyperspectral imaging: calibration problems and solutions”, Chemometrics and intelligent laboratorory systems, Vol. 72, No. 2, JUL 2004, pp. 209-217.

[33] M. E. Klein, B.J. Aalderink, R. Padoan, G. de Bruin, T.A.G. Steemers , “Quantitative hyperspectral reflectance imaging”, Sensors, Vol. 8, No. 9, SEP 2008, pp. 5576-5618.

[34] F.Petrucci “Conservation of painted surfaces: the contribution of image spectroscopy”, Proceedings of the International Workshop SMW08. In Situ Monitoring of Monumental Surfaces. “7-29 October 2008, Florence, Edited by P.Tiano and C.Pardini, Florence, Edifir, pp. 15-20.

[35] M. Attas, E. Cloutis, C. Collins, D. Goltz, C. Majzels, J.R. Mansfield, H.H. Mantsch, “Near-infrared spectroscopic imaging in art conservation: investigation of drawing constituents”, Journal of Cultural Heritage, Vol. 4, No. 2, APR-JUN 2003, pp. 127-136.

[36] P. Carcagni, A. Della Patria, R. Fontana, M. Greco, M. Mastroianni, M. Materazzi, E. Pampaloni, L. Pezzati, “Multispectral imaging of paintings by optical scanning”, Optics and lasers engineering, Vol. 45, No. 3, MAR 2007, pp. 329-336.

[37] B. Hapke, *Theory of Reflectance and Emittance Spectroscopy*, Topics in remote sensing Series editors R. E. Arvidson and M. J. Rycroft, Cambridge University Press, Cambridge, 1993.

[38] K. Nassau, *The Physics and Chemistry of color. The Fifteen causes of color*, John Wiley & Sons, New York, 1983.

[39] J. Schanda (Ed.), *Colorimetry: Understanding the CIE system*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2007.

[40] C. Balas, “ A novel Optical Imaging method for the early detection, quantitative grading and mapping of cancerous and precancerous lesions of the cervix”, IEEE Transactions on biomedical engineering, Vol. 48, No. 1, JAN 2001, pp. 96-104.

[41] G. M. Miskelly, J.H. Wagner, “Using spectral information in forensic imaging”, Forensic Science International, Vol. 155, No. 2-3, DEC 2005, pp. 112-118.

[42] P.B. Garcia-Allende, O.M. Conde, J. Mirapeix, A. Cobo, J.M. Lopez-Higuera, “Quality control of industrial processes by combining a hyperspectral sensor and Fisher's linear discriminant analysis”, Sensors and acuators B: Chemical, Vol. 129, No. 2, FEB 2008, pp. 977-984.

[43] E. Herrala, T. Hyvarinen, O. Voutilainen and J. Lammasniemi, “An optoelectronic sensor system for industrial multipoint and imaging spectrometry”, Sensors and acuators A: Physical, Vol. 61, No. 1-3, JUN 1997, pp. 335-338.

[44] B. Park, K.C. Lawrence, W.R. Windham, D.P. Smith and P.W. Feldner, “Hyperspectral imaging for food processing automation”, Proceedings of SPIE - The International Society for Optical Engineering **,** Vol. 4816, 2002, pp. 308-316.

[45] J. Xing, C. Bravo, T. Pál, H. Jancsók, J. Ramon and Baerdemaeker, “Detecting bruises on ‘golden delicious’ apples using hyperspectral imaging with multiple wavebands”, Biosystems Engineering**,** Vol. 90, No. 1, JAN 2005, pp. 27-36.

[46] G. Zavattini, S. Vecchi, R.M. Leahy, D.J. Smith and S.R. Cherry, “A hyperspectral fluorescence imaging system for biological applications”, Proceedings of the IEEE Nuclear Science Symposium*,* vol. 2, Piscataway, USA, October 19–25 (2003), pp. 942–946.

[47] J.Burger, P. Geladi, “Hyperspectral NIR imaging for calibration and prediction: a comparison between image and spectrometer data for studying organic and biological samples”, The analyst, Vol. 131, No. 10, 2006, pp. 1152-1160.

[48] H.Liang, D. Saunders, J. Cupitt, “A new Multispectral Imaging System for examining paintings”, Journal of imaging science and technology, Vol. 49, No. 6, NOV/DEC 2005, pp. 551-561.

[49] G. Karagianis, C. Salpistis, G. Sergiadis, Y. Chryssoulakis, “Nondestructive multispectral reflectoscopy between 800 and 1900nm: An instrumentfor the investigation of the stratigraphy in paintings”, Review of Scientific Instruments, Vol. 78, No. 6, JUN 2007, pp. 065112.

[50] C. Bonifazzi, P. Carcagni, R. Fontana, M. Greco, M. Mastroianni, M. Materazzi, E. Pampaloni, L. Pezzati, D. Bencini, "A scanning device for VIS-NIR multispectral imaging of paintings", Journal of Optics A: Pure and Applied Optics, Vol. 10, No. 6, Article Number: 064011, JUN 2008.

[51] C.Daffara, E. Pampaloni, M. Barucci, R. Fontana, " Scanning Multispectral IR reflectography SMIIR: An advanced tool for art diagnostics", Accounts of Chemical research, Vol. 43, No. 6, JUN 2010, pp. 847-855.

[52] F. Imai, M. Rosen, R. Berns, "Multispectral imaging of Van Gogh's self-portrait at the national gallery of art, Washington, D.C.", Proceedings *IS&T PICS* Conference, Montreal, Quebec, Canada, 2001, pp. 185-189.

[53] P. Cotte, D. Dupraz, "Spectral imaging of Leonardo Da Vinci's Mona Lisa: A true color smile without the influence of aged varnish", CGIV Final Program and Proceedings, University of Leeds, GB, 2006.

[54] P. Cotte, D. Dupraz, "Spectral imaging of Leonardo Da Vinci's Mona Lisa: An authentic smile at 1523 dpi with additional infrared data", Proceedings *IS&T PICS* Conference Archiving 06, Ottawa, Canada, 2006.

[55] A. Ribés, R. Pillay, F. Schmitt, C. Lahanier, "Studying that smile", IEEE Signal Processing magazine, Vol. 25, No. 4, JUL 2008, pp. 14-26.

[56] R. S. Berns, F. H. Imai, "The use of multi-channel visible spectrum imaging for pigment identification", Vol. I Proceedings of the 13th Triennial ICOM Committee for Conservation, Rio de Janeiro, Brazil, 2002, pp. 217- 222.

[57] M. Bacci, A. Casini, C. Cucci, M. Picollo, B. Radicati, M. Vervat, "Non-invasive spectroscopic measurements on the *Il ritratto della figliastra* by Giovanni Fattori: identification of pigments and colourimetric analysis", Journal of Cultural Heritage, Vol. 4, No. 4, OCT-DEC 2003, pp. 329-336.

[58] CNR-IFAC database, “Fiber Optics Reflectance Spectra (FORS) of Pictorial Materials in the 270-1700 nm range”, http://fors.ifac.cnr.it/

[59] S. Baronti, A Casini, F. Lotti, S. Porcinai, “Principal component analysis of visible and near-infrared multispectral images of works of art”, Chemometrics and intelligent laboratory systems, Vol. 39, No. 1, NOV 1997, pp. 103-114.

[60] S. Baronti, A Casini, F. Lotti, S. Porcinai, “Multispectral imaging system for the mapping of pigments in works of art by use of principal-component analysis”, Applied Optics, Vol. 37, No. 8, MAR 1998, pp. 1299-1309.

[61] C. Balas, “An imaging method and apparatus for the non-destructive analysis of paintings and monuments”, International Patent PCT/GR00/00039.

[62] K. Rapantzikos, C. Balas, “Hyperspectral imaging: potential in non-destructive analysis of palimpsest”, IEEE International Conference on Image Processing, Genova, Italy, September 2005.

[63] J.K. Delaney, E. Walmsley, B. H. Berrie, C. F. Fletcher, “Multispectral imaging of paintings in the infrared to detect and to map blue pigments”, Sackler NAS Colloquium, Scientific Examination of art: Modern Techniques in Conservation and Analysis, Proceedings if the national Academy of Sciences. Washington, 2003, The National Academies press, Washington, D.C., 2005, pp. 120-136.

[64] P. Ricciardi, J.K. Delaney, M. Thoury, M. Facini, “New trends in the in situ analysis of medieval illuminated manuscripts: the use of imaging spectroscopy techniques for improved pigment identification and mapping”, 3rd Course Non-invasive analysis of painting materials, International School Hubert Curien Structural and Molecular Archaelogy, Erice-Sicily (Italy) 14-21 June 2010.

[65] C. Miliani, F. Rosi, B. G. Brunetti, A. Sgamellotti, " In Situ Noninvasive Study of artworks: The MOLAB multitechnique approach", Accounts of Chemical research, Vol. 43, No. 6, JUN 2010, pp. 728-738.

[66] A. Perardi, L. Appolonia, P. Mirti, "Non-destructive in situ determination of pigments in 15th century wall paintings by Raman microscopy", Analytica Chimica Acta, Vol. 480, No. 2, MAR 2003, pp. 317-325.

[67] W.S. Taft Jr., J. W. Mayer, *The science of paintings,* Springer-Verlag, New York, 2000.

[68] P. Seymour, *The Artist's Handbook. A complete professional guide to materials and techniques*, Arcturus Publishing, London, 2003.

[69] J. Peris-Vicente, J. V. Gimeno Adelantado, M. T. Doménech Carbò, R. Mateo Castro, F. Bosch Reig, "Characterization of waxes used in pictorial artworks according to their relative amount of fatty acids and hydrocarbons by gas chromatography", Journal of chromatography A, Vol. 1101, No. 1-2, JAN 2006, pp. 254-260.

[70] S. L. Vallence, "Applications of chromatography in art conservation: techniques used for the analysis and identification of proteinaceous and gum binding media" The analyst, Vol. 122, No. 6, JUN 1997, pp. 75R-81R.

[71] M. Lazzari, O. Chiantore, "Drying and oxidative degradation of linseed oil", Polymer degradation and stability, Vol. 65, No. 2, 1999, pp. 303-313.

[72] P. A. Lewis, *Colorants: organic and inorganic pigments,* in Azimuth, Volume 1 Color for Science, Art and technology, Edited by K. Nassau, Elsevier, Amsterdam, 1998, pp. 283-312.

[73] A. Roy, Editor, *Artist's Pigments*, *A Handbook of their History and Characteristics,* Vol. 2, National Gallery of Art, Washington, Oxford University Press, New York Oxford (1997).

[74] E. West FitzHugh, Editor, *Artist's Pigments*, *A Handbook of their History and Characteristics,* Vol. 3, National Gallery of Art, Washington, Oxford University Press, New York Oxford (1997).

[75] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *Pigment Compendium. A dictionary and optical microscopy of historical pigments*, Elsevier Butterworth-Heinemann, Oxford (2004).

[76] R. L. Feller, Editor, *Artist's Pigments*, *A Handbook of their History and Characteristics,* Vol. 1, National Gallery of Art, Washington, Oxford University Press, New York Oxford (1986).

[77] J. D. Lee, *Chimica Inorganica,* Piccin, Padova (Italia) (2000).

[78] D. Grosjean, P. M. Whitmore, C. P. De Moor, G.R. Cass, J. R. Druzik, "Fading of alizarin and related artists' pigments by atmospheric ozone: reaction products and mechanisms", Environmental Science & Technology, Vol. 21, No. 7, JUL 1987, pp. 635-643.

[79] J. P. Petushkova, N. N. Lyalikova, "Microbiological Degradation of Lead-Containing Pigments in Mural Paintings“, Studies in conservation, Vol. 31, No. 2, MAY 1986, pp. 65-69.

[80] K. Castro, A. Sarmiento, I. Martínez-Arkarazo, J. M. Madariaga, L. A. Fernández, **"**Green Copper Pigments Biodegradation in Cultural Heritage: From Malachite to Moolooite, Thermodynamic Modeling, X-ray Fluorescence, and Raman Evidence", Analytical Chemistry, Vol. 80, No. 11, JUN 2008, pp. 4103-4110.

[81] M. P. Colombini, G. Lanterna, A. Mairani, M. Matteini. F. Modugno, M. Rizzi, " Copper resinate: preparation, characterisation and study of degradation", Annali di Chimica, Vol. 91, No. 11-12, NOV-DEC 2001, pp. 749-757.

[82] R. Newton, S. Davison, *Conservation of glass*, Butterworth Heinemann, Oxford (1989).

[83] M. Mantler, M. Schreiner, “ X-ray analysis of objects of art and archaeology”, Journal of Radioanalitical and Nuclear Chemistry, Vol. 247, No. 3, MAR 2001, pp. 635-644.

[84] Z. Smit, P. Pelicon, G. Vidmar, B. Zorko, M. Budnar, G. Demortier, B. Gratuze, S. Sturm, M. Necemer, P. Kump, M. Kos, “Analysis of medieval glass by X-ray spectrometric method”, Nuclear Instruments and Methods in Physics Research B, Vol. 161, MAR 2000, pp. 718-723.

[85] J. Henderson, *The science and archaeology of materials. An investigation of inorganic materials*, Routledge, London (2000).

[86] G. Scarinci, T. Toninato, B. Locardi, *Vetri*, Casa Editrice Ambrosiana, Milano (1977).

[87] P. Mirti, P. Davit, M. Gulmini, “Colourants and opicifiers in seventh and eighth century glass investigated by spectroscopic techniques”, Analytical and Bioanalytical Chemistry, Vol. 372, No. 1, JAN 2002, pp. 221-229.

[88] G. Fuxi, *Optical and Spectroscopic properties of glass*, Springer, Berlin (1992).

[89] C. Fiori, M. Vandini, V. Mazzotti, *I colori del vetro antico. Il vetro musivo bizantino*, Il prato casa Editrice Saonara, Padova (Italia) (2004).

[90] C. R. Bamford, *Colour Generation and Control in Glass. Glass Science and Technology,2*, Elsevier Scientific Publishing company, New York (1977).

[91] W. A. Weyl, *Coloured Glasses*, Society of Glass and Technology Sheffield (UK), 6th edition, (1999).

[92] H. Scholze, *Le verre. Nature, structure et propriétiés*, Institut du verre Paris, Paris, 2ème edition , (1980).

[93] N. Carmona, M. Oujja, E. Rebollar, H. Römich, M. Castillejo, "Analysis of corroded glasses by laser induced breakdown spectroscopy", Spectrochimica Acta Part B, Vol. 60, No. 7-8, AUG 2005, pp. 1155-1162.

[94] F. Barbana, R. Bertoncello, L. Milanese, C. Sada, "Alteration and corrosion phenomena in Roman submerged glass fragments", Journal of Non-Crystalline Solids, Vol. 337, No. 2, JUL 2004, pp. 136-14.

[95] B. Dal Bianco, R. Bertoncello, L. Milanese, S. Barison, "Glasses on the Seabed: Surface Study of Chemical Corrosion in Sunken Roman Glasses", Journal of Non-Crystalline Solids, Vol. 343, No. 1-3, SEP 2004, pp. 91-100.

[96] http://www.specim.fi

[97] http://www.labsphere.com/

[98] A. Galli, G. Poldi, M. Martini, E. Sibilia, C. Montanari, L. Panzeri, "Study of blue colour in ancient mosaic tesserae by means of thermoluminescence and reflectance measurements", Applied Physics A - Materials Science & Processing, Vol. 83, No. 4, JUN 2006, pp. 675-679.

[99] P. Croveri, I. Fragalà, E. Ciliberto, " Analysis of glass tesserae from the mosaics of the 'Villa del Casale' near Piazza Armerina (Enna, Italy). Chemical composition, state of preservation and production technology", Applied Physics A - Materials Science & Processing, Vol. 100, No. 3, SEP 2010, pp. 927-935.

[100] B. Dal Bianco, "Study on the use of sol-gel silica to simulate the weathering of ancient glass", Doctoral Dissertation of the Università degli Studi di Padova (Italia), (2006).

[101] http://kremer-pigmente.de/en

[102] S. Rinaldi, *La fabbrica dei colori, pigmenti e coloranti nella pittura e nella tintoria*, Ed. Il Bagatto, Roma (1986).

[103] M. Elias, C. Chartier, G. Prévot, H. Garay, C. Vignaud, “The colour of ochres explained by their composition”, Materials Science & Engineering B, Vol. 127, No. 1, FEB 2006, pp. 70-80.

[104] G. Dupuis, M. Elias, L. Simonot, “Pigment Identification by Fiber-Optics Reflectance Spectroscopy”, Applied Spectroscopy, Vol. 56, No. 10, OCT 2002, pp. 1329-1336.

[105] D. Hradil, T. Grygar, M. Hruskova, P. Bezdicka, K. Lang, O. Schneewiss, M. Chvatal, “Green earth pigment from the Kadan region, Czech Republic: Use of rare Fe-rich smectite”, Clays and Clay minerals, Vol. 52, No. 6, DEC 2004, pp. 767-778.

[106] D. Hradil, T. Grygar, J. Hradilova, P. Bezdicka, “Clay and iron oxide pigments in the history of painting”, Applied Clay Science, Vol.22, No. 5, APR 2003, pp. 223-236.

[107] M. Matteini, A. Moles, *La chimica nel restauro. I materiali dell’arte pittorica,* Nardini, Firenze (1999).

[108] C. Patton (Ed.)*, Pigment Handbook. Volume I: Properties and Economics,* John Wiley, New York (1973).

[109] D.A. Scott, *Copper and Bronze in Art. Corrosion, Colorants, Conservations.,* Getty Publications (2002).

[110] M. Meyer, P.Bonomi da Monte, *Colori e Vernici. Manuale ad uso dei Pittori, Verniciatori, Ebanisti e Fabbricanti di colori e vernici.,* Ulrico Hoepli, Milano (1913).

[111] E. B. Faulkner, R. J. Schwartz (Eds.), *High Performance Pigments*, WILEY-VCH Verlag WILEY-VCH Verlag GmbH & Co. KGaA,, 2nd edition, Weinheim (2009).

[112] R. Arbizzani, U. Casellato, E. Fiorin, L. Nodari, U. Russo, P.A. Vigato, “Decay markers for the preventative conservation and maintenance of paintings”, Journal of Cultural Heritage, Vol. 5, No. 2, APR-JUN 2004, pp. 167-182.

[113] R. Mayer, *The artist s Handbook of Materials and Techniques,* Viking Penguin, New York (1991).

[114] D. Scalarone, M. Lazzari, O. Chiantore, “Thermally assisted hydrolysis and methylation-pyrolysis-gas chromatography/mass spectrometry of light-aged linseed oil”, Journal of analytical and applied pyrolysis, Vol. 58, APR 2001 , pp. 503-512.

[115] http://www.lefranc-bourgeois.com/beaux-arts/

[116] C. Altavilla, E. Ciliberto, “Copper resinate: an XPS study of degradation”, Applied Physics A. Materials & processing, Vol. 83, No. 4, JUN 2006 , pp. 699-703.

[117] L. Cartechini, C. Miliani, B.G. Brunetti, A. Sgamellotti, C. Altavilla, E. Ciliberto, F. Dacapito, “X-ray absorption investigations of copper resinate blackening in a XV century Italian painting”, Applied Physics A. Materials & processing, Vol. 92, No. 1, JUL 2008 , pp. 243-250.

[118] P. Matteini, M. Camaiti, G. Agati, MA Baldo, S. Muto, M. Matteini, “Discrimination of painting binders subjected to photo-ageing by using microspectrofluorometry coupled with deconvolution analysis”, Journal of Cultural Heritage, Vol. 10, No. 2, APR-JUN 2009 , pp. 198-205.

[119] E. Marengo, M. C. Liparota, E. Robotti, M. Bobba, “Monitoring of paintings under exposure to UV light by ATR-FT-IR spectroscopy and multivariate control charts”, Vibrational Spectroscopy, Vol. 40, No. 2, MAR 2006, pp. 225-234.

[120] E. Marengo, M. C. Liparota, E. Robotti, M. Bobba, M. C. Gennaro, “Monitoring of pigmented surfaces in accelerated ageing process by ATR-FT-IR spectroscopy and multivariate control charts”, Talanta, Vol. 66, No. 5, JUN 2005, pp. 1158-1167.

[121] M. Bacci, M. Picollo, S, Porcinai, B. Radicati, “Evaluation of the museum environmental risk by means of tempera-painted dosimeters”, Termochimica acta, Vol. 365, No. 1-2, DEC 2000, pp. 25-34.

[122] Y. Brik , M. Kacimi, M. Ziyad , F. Bozon-Verduraz, “Titania-supported cobalt and cobalt-phosphorus catalysts: Characterization and performances in ethane oxidative dehydrogenation”, Journal of catalysis, Vol. 202, No. 1, AUG 2001, pp. 118-128.

[123] E. Ioakimoglou, S. Boyatzis, P. Argitis, A. Fostiridou, K. Papapanagiotou, N. Yannovits, “Thin-film study on the oxidation of linseed oil in the presence of selected copper pigments”, Chemical of materials, Vol. 11, No. 8, AUG 1999, pp. 2013-2022.

[124] A. A. M. Farag, “Optical absorption studies of copper phthalocyanine thin films”, Optics & Laser technology, Vol. 39, No. 4, JUN 2007, pp. 728-732.

[125] G. C. Holst and T. L. Lomheim, *CMOS/CCD sensors and camera systems*, JJCD Publishing/SPIE Press, Washington (2007).

[126] http://www.labsphere.com/products/reflectance-materials-and-coatings/high-reflectance-materials/optical.aspx

[127] J. Burger, P. Geladi, “Hyperspectral NIR image regression part 1: Calibration and correction”, Journal of Chemometrics, Vol. 19, No. 5-7, MAY-JUL 2005, pp. 355-363.

[128] A. Springsteen, “Standards for the measurement of diffuse reflectance - an overview of available materials and measurement laboratories”, Analytica chimica acta, Vol. 380, No. 2-3, FEB 1999, pp. 379-390.

[129] F.Grum, G.W.Luckey, “Optical Sphere paint and a working standard of reflectance”, Applied Optics, Vol.7, No. 11, NOV 1968, pp. 2289-2294.

[130] E.R.Young, K.C. Clark, R. B. Bennet, T. L. Houk, “Measurement and parameterization of the bidirectional reflectance factor of $BaSO_4$ paint”, Applied Optics, Vol.19, No. 20, OCT 1980, pp. 3500-3505.

[131] T.Takahashi, Y.Ikezawa, “White standard paint”, United States Patent US 6555608 B2, 2003.

[132] http://www.saint-gobain-glass.com/saint-just/VSJ_GB/index.asp

[133] M. Bacci, M. Picollo, "Non-destructive spectroscopic detection of cobalt(II) in paintings and glass", Studies in conservation, Vol. 41 No. 3, 1996, pp. 136-144.

[134] Cennino Cennini, *Il libro dell'arte*, Neri Pozza editore, Vicenza (2009).

[135] C. Danti, M. Matteini, A. Moles, *Opificio delle pietre dure e laboratori di ristauro di Firenze. Le pitture murali. Tecniche, problemi, conservazione,* Centro di della Edifimi, Firenze (1990).

[136] F. Rosi, A. Daveri, C. Miliani, G. Verri, P. Benedetti, F. Pique, B. G. Brunetti, A. Sgamellotti, "Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach", Analytical and bioanalytical chemistry , Vol. 395, No. 7, DEC. 2009 pp. 2097-2106.

[137] P. Mora, L. Philippot, *La Conservazione delle pitture murali*, Bresciani, Milano (2001).

[138] http://www.ctseurope.com/

[139] http://www.dolcicolor.it/

[140] V. Terribile Wiel Marin, G. Zampieri, *Giuseppe Tartini e la Chiesa di Santa Caterina a Padova. Archeologia Storia Arte intorno alla Chiesa di Santa Caterina d'Alessandria. Risultati delle ricognizioni scientifiche delle tombe di Giuseppe Tartini, di Luigi Calza, dei Parroci e degli studenti legisti,* Grafiche Turato sas Rubano, Padova (1999).

[141] N. Crivellaro, "Approfondimento della conoscenza del dipinto murale sito presso l'ex convento di S. Caterina di Padova mediante indagini scientifiche e storico-artistiche", Tesi di laurea specialistica del corso Scienze e Tecnologie per i Beni archeologici e artistici, Università degli studi di Padova (Italia), (2009-2010).

[142] http://www.arcadiaricerche.it/

[143] D.M Sherman, T. D. Waite, “Electronic spectra of Fe^{3+} oxides and oxide hydroxides in the near IR to near UV”, American Mineralogist, Vol. 70, No. 11-12, NOV-DEC 1985 pp. 1262-1269.

[144] J. Torrent, V. Barron, “The visible diffuse reflectance spectrum in relation to the color and crystal properties of hematite”, Clays and Clay minerals, Vol. 51, No. 3, JUN 2003, pp. 309 - 317.

[145] C. R. Bamford, “The application of the ligand field theory to coloured glasses”, Physics and Chemistry of glasses, Vol. 3, No. 6, DEC 1962, pp.189-202.

[146] Yu. A. Guloyan, “Complete analysis of ionic staining of glasses by transition-metal compounds”, Glass and ceramics, Vol. 64, Nos. 5-6, MAY 2007, pp. 153-158.

[147] S. P. Singh, A. Tarafder, A. Tarafder , “Comparative investigation on the effect of alkaline earth oxides on the intensity of absorption bands due to Cu^{2+}, Mn^{3+} and Cr^{3+} ions in ternary silicate glasses”, Bulletin of materials science, Vol. 27, No. 3, JUN 2004, pp. 281-287.

[148] A. Lopez-Delgado, E. Cano, J. M. Bastidas,F. A.Lopez, “A laboratory study of the effect of acetic acid vapor on atmospheric copper corrosion”, Journal of the electrochemical society, Vol. 145, No. 12, DEC 1998, pp. 4140-4147.

Acknowledgements

First of all, I would like to thank the group of chemistry of cultural heritage, prof. Bertoncello, prof. Russo, Dr. Dal Bianco, Valentina Donà, Andrea Vezzoli and Nicola Crivellaro to support me during these research work. I have to give a special THANKS to Dr. Voltolina, Dr. Nodari and Matteo Monti for being not only work colleagues but also good friends.

This research would have not been possible without the collaboration and help of Dr. Poletto and Ing. Ratti of the LUXOR laboratory, which have developed and built the instrument and that had worked intensively with me. I would like to thank prof. Cortelazzo, Dr. Paviotti and Carlo Tona.

I have to express gratitude to prof. Zanonato for some materials, instruments and advices. I would like to thank Dr. Armelao, Dr. Gross, Nicola Tiso, prof. Santi, prof. Zecca and Elena Campadello.

I would like to express my deeply thankfulness to Piero e Matia Modolo, for their advises and materials regarding stained glass windows and their extreme helpfulness.

The interdisciplinary study of the mural painting of Santa Caterina was performed by the collaboration of the CARIPARO and the *Fondazione I.R.P.E.A.*. A special thanks to all the personal of the Biblioteca di Sciencze Statistiche, specially to its director prof. Giorgio Celant and to Elena dal Moro for their helpfulness.

I am deeply grateful for the material and spiritual support that my parents, brothers and all my family have given me, and a special gratitude to my “cuadrilla” that have supported and “sopported” me since a long long time….

Thanks to my “translators”…Dr.Voltolina (poliglota…) and Rafael, you have saved me from myself!

I have spent the last three years in Padua and the people that I had known here had become my “Veneto” family….thank you all….Thanks to all the members of the ENTERPRISE, Dr. Wolf, Dr. Cucciolotto, Dr.ssa FAMENGO and Dr. (captain) Galenda….it has been wonderful being a furlan/triestina with all of you…Thanks to Dr. Maxbauer and its wonderful dinners and cocktails, Dr. Donoli who had “pump” me confidence, Dr. Montagner and his “ultimi”, Dr. Fresch and the pastis, Ricki, Mirko, Luca R., Eddie, Patty, Borgogno, Antolini, Aronna, Aronne, Gabri…. I would like to thank Enzo for all his help in many ways. Thanks to Chiara and Silvia M., my personal doctor….

Finally, I would like to thank Enrico who has feed me brunch type all this period avoiding my starvation….thank you…**E**scusa…thank you…

Thank you!...Gracias!…Grazie!…Eskerrik asko! (este va por ti tita!)