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Pigment Identification of Paintings Based on Kubelka--Munk Theory and Spectral Images

Farhad Moghareh Abed

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Pigment Identification of Paintings Based on Kubelka-Munk Theory and Spectral Images

by

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B.S. Isfahan University of Technology, 2002
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A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of Doctorate of Science in Color Science

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Pigment Identification of Paintings Based on Kubelka-Munk Theory and Spectral Images

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ABSTRACT

The preservation of cultural heritage and treatment thereof are delicate responsibilities that demand the best possible technologies and extreme care to avoid any irreversible loss. It necessitates a deep understanding of constituent materials, along with the analytical methods and cutting-edge technologies. Considering this direction, the goal of this dissertation is to promote the conservation procedures by providing an applicable workflow for spectral-based pigment identification. The proposed pipeline is a novel and practical aid for museum conservators for many aspects, such as inpainting, treatment and archiving of artwork.

Spectral-based pigment identification algorithms rely on accurate spectral data, a subtractive mixing model and an effective unmixing algorithm. In this dissertation, the spectral data were obtained using a spectral image acquisition system as a feasible and non-destructive technique. A liquid-crystal tunable filter (LCTF) and a CCD camera were used for spectral measurement of the painting. The spectral accuracy and precision of the LCTF-based spectral acquisition system were assessed and enhanced. Of the common factors affecting the acquisition performance,
capturing geometry, LCTF angular dependencies and spectral characterization algorithm were new contributions to the traditional workflow.

The complexity of subtractive mixtures limits the effective application of linear unmixing algorithms for pigment identification. Accordingly, a new linear modification of single-constant Kubelka-Munk theory was derived to enable the use of available linear spectral unmixing algorithms for paint mixtures. A selection of geometric and iterative-based unmixing algorithms was applied to the LCTF spectral images in the subtractive mixing space using the defined subtractive linear model. Final sets of primary pigments were improved employing a pre-existing database of common pigments as a tool for practical inpainting procedures. The pigment maps, showing the concentration of each pigment per pixel, and RMS error images were calculated after estimating the primary pigments. The estimation errors and the performance of the pigment selection algorithms were assessed using 23 validation paintings.

Finally, the primary pigment information combined with multi-spectral images from a commercial 6-channel imaging system was used for visualization and high-resolution spectral image reproductions.
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CHAPTER 1: INTRODUCTION

The preservation of cultural heritage, and treatment thereof, is a delicate responsibility that demands the best possible technologies and extreme care to avoid any irreparable loss. It necessitates a deep understanding of constituent materials, along with the analytical methods and cutting-edge technologies. Considering this direction, the goal of this dissertation is to promote the conservation procedures by providing a practical workflow for pigment identification based on a sophisticated spectral imaging of an LCTF-based multispectral camera as an extension of previous research by Zhao (Zhao, 2008).

Spectral imaging is turning into an exclusive state-of-the-art, non-invasive technology in museums for spectral analysis of paintings (Cappellini, and Piva, 2006). It also benefits from distinct information of the surface visual appearance as a key element in archiving and virtual simulations of paintings in museums. Today, spectral imaging is a prior candidate for a definitive record of the state of the object for purposes such as visualizations and reproductions of artworks, inpainting, restoration, documentation, conservation and addressing metamerism (Martinez, et al., 2002; Barni, et al., 2005; Berns, 2005; MacDonald, 2006; Tominaga, 2012). It eases assessment and monitoring of deteriorations of the artwork over time,
artwork relocation and conservation treatment. Accurate and spectral reproduction of artwork facilitates further studies and dissemination without the risk of damaging the artwork or the need to move the original piece. Spectral imaging also aids conservators to detect changes over time. Additionally, it facilitates accurate colorimetric and spectral reproduction of the artwork for high quality documentation and dissemination (Haneishi, et al., 2000; Berns, 2001; Imai, et al., 2001; Cheung, et al., 2004b; Cappellini, and Piva, 2006; Fischer, and Kakoulli, 2006; Bianco, et al., 2011; Tominaga, 2012).

A significant use of spectral measurements is in material diagnosis and pigment identification of paintings (Tominaga, 2012). The process assists conservators and restorers in choosing appropriate maintenance procedures and pigment palettes for inpainting, treatment and conservation processes (Cappellini, and Piva, 2006). A summary of applications of multispectral imaging in museums is outlined in Figure 1.1. The combination of spectral data along with the pigment information form the basic input material for most of the latter analyses and studies.

![Figure 1.1: A general workflow of multispectral image acquisition systems and its applications for conservation.](image)

Unlike spectral data, pigment information cannot be measured easily. Pigment identification refers to the algorithms by which the constituent pigments of a painting are extracted. In image-based pigment identification methods, the pigment
data are obtained from a spectral image of the artwork that is analogous with the spectral unmixing methods used in the remote sensing and geographic information system (GIS) fields for decomposing a given mixture to a collection of spectral primaries, called endmembers. The procedure also includes estimating the portion (or abundances) of each one of the endmembers present in each pixel. Similar to image-based pigment identification methods, endmembers in remote sensing generally correspond to materials such as different kinds of soil, water, metal, vegetation, etc.

Most of the practical unmixing algorithms assume convexity and linearity of the mixing model. Unfortunately, such algorithms do not describe spectral subtractive mixtures. Among the common subtractive mixing models, single-constant Kubelka-Munk (KM) theory is the first candidate promising a linear model for opaque surfaces. Unfortunately, single-constant KM theory does not follow convexity and loses its validity for high concentrations of pigments, which is a common case for paintings. On the other hand, the original form of the KM theory, also called two-constant Kubelka-Munk theory, is a non-linear and a rather complicated model but gives a better estimation of subtractive mixtures. All of these limitations make the choice of an appropriate subtractive mixing model a challenging task. Convexity and linearity, as well as an accurate description of subtractive mixtures, are viable traits for image-based pigment identification algorithms of subtractive mixtures. Meanwhile, pigment identification algorithms demand a certain level of spectral accuracy as a effective factor influencing the efficiency of results (Berns, and Imai, 2002).

Applicability, software implementation and visualization of the algorithms on actual image artwork are other important aspects of an applicable spectral-imaging paradigm. Virtual demonstration and editing of the artwork provide simulations of a variety of the treatments, particularly when manipulation of the artwork is not practical. Moreover, some visualizations are merely limited to digital simulations of the painting, such as color reconstruction of a faded pigment in a particular painting.
This dissertation is defined according to the need of a practical workflow for spectral measurement, pigment identification and visualization of paintings based on an LCTF-based multispectral acquisition system. The implementation involves empirical solutions for 1) acquiring a more accurate multispectral measurement workflow for pigment identification; 2) evaluating and developing a linear subtractive mixing model for paint layers; and 3) implementing a practical unmixing solution suitable for pigment identification. Finally, a useful way of visualization and simulation of the painting’s spectral images is introduced.

1.1 Dissertation outline

This dissertation is organized as follows. First, a general introduction of pigment identification methods, spectral images and unmixing methods is provided in Chapter 2. It is then followed by evaluating camera characterization and the LCTF multispectral capturing system to acquire spectral images in Chapters 3. Next, the applicability of the KM subtractive mixing theory is examined for pigment identification in Chapter 4. It covers the development and evaluation of a new linear subtractive mixing theory for pigment identification. Chapter 5 allocated to evaluations and development of unmixing algorithms to the spectral images for pigment identification. In Chapter 6, practical implementation of the algorithm for high-resolution images is introduced. Finally, Chapter 10 contains the dissertation conclusions and future work.
CHAPTER 2: LITERATURE REVIEW

Pigment information and surface spectral data are interrelated in subtractive mixtures. The spectral information for the constituent pigments of a particular painting can be estimated using spectral imaging. On the other hand, spectral data obtained from a spectral imaging system can be enhanced using primary pigment information. There are several of techniques available for acquiring both spectral and pigment information, none of which should be neglected for satisfactory analyses.

Artistic and historical data might be considered the primitive source of pigment identification. Each artist has his or her own style of mixing, painting and using materials in their art over a specific period of time or in a particular location. This information is beneficial for selecting appropriate databases and methods for further material diagnoses and pigment identifications. Other sorts of analytical methods are categorized into two categories: invasive and non-invasive. Non-invasive methods allow analytical data to be extracted without any damage or sample taking of the artwork, which is specifically preferred by museums. Conversely, invasive methods require a sample, albeit very small, of the object being examined. The invasive method may not damage the evaluated piece itself, but it
cannot be performed in situ. The examined piece, however, can be used for other invasive assessments in later steps. The advantages of the methods are their sensitivity and discrimination accuracy. The sampling procedure itself is a challenging and delicate step of the invasive analytical approaches including issues such as sufficient size, location and shape of the sample for an acceptable degree of diagnosis precision.

The optimal choice of the analytical techniques is different with case. Typically, a combination of several techniques is used in order to reach the desired accuracy and overcoming sampling obstacles. Non-invasive and non-contact measurements are obvious safer alternatives as opposed to those that need sample-taking. A particular and difficult instance is to a take an appropriate sample from a painting when it is varnished.

2.1 Analytical Methods for Pigment Identification in Museums

There are a wide variety of analytical techniques available for pigment identification. Below is a summary of the most common non-invasive and micro-invasive analytical methods over and above multispectral imaging, each of which can be studied more extensively, beyond this dissertation. For more information on these methods, see Refs. (Ciliberto, and Spoto, 2000; Bacci, et al., 2001; Bruni, et al., 2002; Pinna, et al., 2009):

2.1.1 Optical Microscopy

Optical Microscopy is a preliminary method of examining paintings and is categorized as a non-invasive method, particularly with the aid of fiber optic equipment. Typically, different types of illuminations are employed for better discrimination and identification purposes. Observing the specimen under ultra violet (UV) radiation helps the examiner to make more precise interpretations of the florescent materials. UV radiation is a useful way of distinguishing zinc and titanium white as they behave differently in UV illuminations. Another option is using polarized light to attain information on the crystallographic structure of the
materials. This method is not classified as an advanced pigment identification method due to its limitations and operational requirements. The extracted data of this technique are narrowed to surface morphology and superficial observations.

2.1.2 X-Ray Fluorescence (XRF)

XRF is an analytical technique by which different elements of the sample are indicated according to the fluorescent radiations of the elements with respect to incident high-energy X-rays or gamma rays. The incident X-ray is capable of expelling electrons from inner orbitals setting the atom structure in an unstable form. Expelled electrons in higher orbitals fall back into the lower orbital to form a stable structure. In the falling process, a specific pattern of energy is released in the form of photons. These radiated photons can be initiators of a secondary fluorescent radiation. Eventually, an integration of the fluorescent radiations forms a particular distribution of photons (X-ray lines) being utilized to determine the elemental composition of the specimen.

Depending on the energy involved, incident X-ray penetrates to either a thin superficial or deeper layers of the material. This technique is commonly applied to the samples in the form of powder, but for identification purposes it is also performed to works of art in situ and as a non-invasive and harmless technique.

According to the fundamentals of the technique, the analysis is limited to elemental components as opposed to the chemical states or molecular structures. As a result, components with similar elements but a different chemical structure cannot be separated. In addition, detecting and extracting the radiated ray become more difficult when light elements produce low-fluorescence radiation. The radiated fluorescent light might be absorbed or produce similar X-ray lines prone to overlapping for such elements. The mentioned limitations particularly influence the process of accurate pigment identification in artworks because of the presence of organic and light elements. Varnish is another factor weakening the amount of
detecting X-ray light. Furthermore, analyzing XRF information can be noticeably complicated when it is applied to the deeper layers within materials.

Particle-included X-ray emission (PIXE) is another non-destructive technique analogous to XRF, but the stimulation is performed by a beam of charged particles. PIXE also shares similar difficulties for analyzing complex paint and varnished layers.

2.1.3 X-Ray Diffraction (XRD)
XRD is a non-invasive method capable of being applied to paintings in situ. In this technique, the sample is radiated by a monochromatic X-ray and the scattered beam reflected is measured in different angles. The detected signals are dissimilar corresponding to the diffracted light associated with the crystal structure. Consequently, this technique is beneficial only for identifying of crystalline materials. The specimen, therefore, should not contain high amounts of absorption within the emitted X-ray frequencies. The data from this technique are usually combined with that from XRF (as an elemental method) to predict the full molecular structure of the materials.

2.1.4 Fourier Transform Infrared Spectroscopy (FTIR)
The infrared region of the electromagnetic spectrum corresponds with the energy of most molecular vibrations. Vibration frequencies are detected and analyzed in order to identify organic and inorganic materials. Based on the materials under examination, mid-infrared (MIR), near-infrared (NIR) or far-infrared (FIR) regions are utilized for material diagnosis. Regular FTIR methods are divided into transmission and reflection modes, both of which require a small sample for analysis and therefore are micro-destructive methods. However, a non-invasive, non-contact and portable FTIR by fiber optics has become available recently, making this method promising for evaluating paintings in museums. Portable FTIR works in the reflective mode and is limited to the mid-FTIR range. This limitation influences the performance in terms of reliability in identifying a narrow range of materials such as silicates, carbonates, sulphates, etc. Further limitations rise due to
the overlap of absorption bands, so-called matrix effect, which manifests in the spectral mode when the paint surface is evaluated directly. In addition, acquired spectra in the spectral mode are distorted, depending on the band intensity, sample concentration and measurement system’s optical layout. Consequently, the spectral form reflective mode cannot be compared to that obtained in transmission mode. As a result, interpreting the FTIR spectrum of paint layers with complex pigment mixtures cannot be carried out easily.

2.1.5 Raman Spectroscopy

Raman spectroscopy, or Raman Micro-Spectroscopy, can be employed to identify a wide variety of organic and inorganic materials, such as synthetic or natural pigments, amorphous or crystallized. Raman spectroscopy is a structural analytical technique based on illuminating the sample by a line (or monochromatic) light source, usually in UV-Vis-IR regions, and measuring the scattered light with a spectrometer. When the light collides with a molecule of the sample, the scattered radiation has either the same or dissimilar frequencies with respect to the frequency of the incident light. For elastic collision, incident and scattered radiation has the same frequency, which is also called Rayleigh scattering. Conversely, for an inelastic collision, the scattered light changes its frequency according to the vibration and rotational levels of the molecules. The radiations close to the incident light, related to elastic Rayleigh scattering, is removed and the reminded light is used for material identifications. Raman spectroscopy measurements can be applied to powder samples (in micro scale) or directly to the artwork (in-situ) without any particular preparation. Hence, this method is also considered as a non-invasive method.

Interpretation of Raman spectrometry is accomplished using a pre-existing database of materials. Each specific molecular structure produces a certain Raman curve like a fingerprint. The molecular characteristic of the sample is indicated by comparing the measured Raman spectral with a pre-measured database of a wide variety of materials including pigments. The comparisons are rather simple if the
sample is made of pure materials. Complex mixtures of materials, on the other hand, result in a more complicated Raman spectral curve and are more difficult to interpret. Another limitation of this technique is fluorescence emissions of the sample, which hamper an accurate analysis.

2.1.6 Computed Tomography (CT)

In CT, a three-dimensional model of the surface is attained according to the detected signal incident in multiple angles. The intensity of the signal from the detector corresponds to the amount of the radiations (that can be X-rays, gamma rays, neutrons or ultra-sound) absorbed or scattered by the material under examination for each angle. An image reconstruction algorithm is then used to reconstruct the images to form a three-dimensional model of the material.

The method can be applied to the painting to extract some information about the internal structure of the paint layers useful for material identifications. Type and the intensity of the incident radiation are optimized based on the substrate and thickness of the paint layers. However, paintings with thick layers, particularly wooden supports, overshadow the measurements. When the substrate is thicker than the paint layers, the acquired signal of the paint layers is influenced by that of the substrate, which limits the applicability of the technique. The measurement procedure, including rotating the painting so that incident radiations can be projected and collected in different directions, can be difficult when the painting is large.

2.1.7 Other Analytical Methods

There are other analytical methods based on the physical and chemical background of the materials, such as thermal analysis, liquid chromatography, gas chromatography, spot and staining, most of which need micro-sampling for examinations. These methods can be applied to a very small sample or a cross-section collected from the paintings. Obviously, non-invasive techniques are still preferred by museums.
In the next section, multispectral imagery as a non-invasive method is discussed. Multispectral imagery is the principle method for pigment identification in this dissertation. Although other analytical methods can provide considerable auxiliary information, it is assumed that collected spectral data are the only source for the analysis.

2.2 Multispectral Measurement

In a multispectral capturing system, the spectral radiance of the scene is under sampled into a lower dimension. Every pixel in a spectral image is a vector representing a projection of spectral radiance with respect to space associated with the spectral sensitivity of the device’s sensor, illumination and transmission of the filters (Figure 2.1). The number of components per pixel can be as few as three and as many as several hundred bands for hyper-spectral images. Obviously, increasing the number of capturing channels yields more information of the surface spectral reflectance, which then demands more sophisticated equipment. In addition, further combinations of multispectral channels result in higher accuracy in colorimetric reproductions (Cheung, et al., 2004b). Most of the multispectral capturing systems in museums sample the spectral data in the visible range of electromagnetic spectrum due to the color discrimination of spectral shapes; however some of the capturing systems are also equipped to cover UV and IR areas for further examinations. The output of the capturing systems is a series of images corresponding to each one of the spectral bands. The entire output can be interpreted as a data cube that includes a stack of two-dimensional images integrated over a range of wavelengths (Keshava, and Mustard, 2002; Manolakis, et al., 2003).
The development of multispectral imaging technology began about 40 years ago in the fields of astrophysics, remote sensing and medicine. This technology became more accessible after undergoing rapid development from the early 1990s to become applicable in other fields of research such as art conservation and examination (Fischer, and Kakoulli, 2006). The technology can be considered an extension of traditional trichromatic acquisition devices to higher dimensions. Multispectral systems provide finer sampling of spectral reflectance facilitating more accurate spectral reflectance estimations for each pixel, as well as addressing the issue of metamerism and faithful color reproduction for different viewing conditions (MacDonald, 2006).

One simple approach for spectral imaging is to measure the full spectral information for each point on the painting, so called direct measurement or complete spectral scanning. Three basic configurations for a full spectral sampling are point, line and focal plane scanning imaging. In all three methods, the spectral information of each
pixel of the image is measured independently (Geladi, et al., 2007). In contrast, indirect methods refer to sub-sampling of spectral reflectance together with some spectral estimation algorithms. Each one of the methods has pros and cons considering the spectral and colorimetric accuracy, cost, speed, hardware and software complexity, and maintenance of the equipment (Berns, 2005). In some other categories the multispectral imaging systems are divided into passive and active illumination. In passive illuminations the filtration mechanisms are placed in front of the camera sensor, which is popular in most conventional equipment. In active spectral imaging method, the filtration layout is applied to light source by direct filtering or utilizing a programmable light source. This configuration expedites the capturing speed compared to the passive methods (Tominaga, 2012). Below is a summary of the different available methods, along with common equipment for conservation purposes.

Multi-filter capturing systems are divided into narrow-band and wide-band depending on the subsampling bandwidth (Imai, et al., 2000; Bianco, et al., 2011). Narrow-band filters enable more precise and independent sampling of spectral reflectance, thus making the spectral estimations more convenient. Positioning a set of narrow-band optical or interference filters in front of the camera (using an electro-mechanical wheel for instance) is a simple and classic way of building a narrow-band-based spectral imaging system (Sugiura, et al., 2000; Yamaguchi, et al., 2001; Helling, et al., 2004; Tominaga, et al., 2004; Fukuda, et al., 2005; MacDonald, et al., 2013). Some of the practical drawbacks of this approach limits its functionality including time consuming measurements, further image registration, a non-versatile number of filters, the cost of custom-made filters and misalignment issues (Novati, et al., 2005; Fischer, and Kakoulli, 2006; Bianco, et al., 2011; MacDonald, et al., 2013). Liquid Crystal Tunable Filters (LCTFs) or Acousto-Optical Tunable Filters (AOTFs) are convenient replacements for color wheels. The transmission of a LCTF can be controlled electronically by modulating the voltage of the acoustic signal. An LCTF has more flexibility in making arbitrary spectral shapes with finer spectral sampling without moving the capturing unit and a reasonable switching time. The
necessity of large storage capacity, complexity, cost, lower signal to noise ratio (SNR) and unwieldiness are other drawbacks of LCTF-based imaging systems. In addition, LCTFs usually have low transmission in shorter wavelengths of light (blue and ultraviolet), which lowers the SNR in combination with silicon sensors and light sources with low correlated color temperatures. Small SNR capacity specifically makes high spatial resolution imaging difficult when a full image is captured (Taplin, and Berns, 2005; Fischer, and Kakoulli, 2006; Bianco, et al., 2011).

In wide-band filter-based systems, spectral reconstruction algorithms are required for spectral imagery. This process necessitates more calibration measurements and complicated mathematical algorithms. These imaging systems are comparatively cheaper, more flexible and easier to setup, and attain larger SNR for capturing spectral images in higher spatial resolutions. It has been also reported that wide-band filters can lead to comparable performance to the narrow-band filters (Imai, et al., 2000). The selection of the optimum number and the spectral properties of filters affect the estimations significantly, leading to large amount of research on evaluating and selecting the optimum number of filters and transmission curves; however, no official standards have been developed as yet (Imai, et al., 2003; Taplin, and Berns, 2005; Fischer, and Kakoulli, 2006; Bianco, et al., 2011). Another approach is to evaluate and extract an optimized combination of available commercial filters for spectral reconstruction (Schmitt, et al., 1999; Haneishi, et al., 2000; Cheung, et al., 2004b).

Combining a set of wideband filters with trichromatic digital camera is an inexpensive alternative to forming a high-speed narrow-band sampling acquisition for high-resolution spectral imagery. The combination of high-resolution trichromatic detector and bandpass filters generate an adequate number of spectral images with reasonable number of capturing shots. The registration processes is also more convenient compared with previous techniques. The accessibility of high-resolution and professional-quality digital cameras for capturing turns these systems to be economical, fast, easy to set up and more practical. A comprehensive
A literature review and comparisons of available capturing multispectral imaging systems can be found in Chapter 5 of ref (Sun, 2010).

Fiber optics reflectance spectroscopy (FORS) provides a high-resolution spectral reflectance for a particular region or spot of the sample for validation or interpolation of multi-spectral results (Berns, et al., 2002; Fischer, and Kakoulli, 2006). The spot spectral measurements can be expanded to a full multi-spectral imaging system by combining the point spectrophotometer and a scanning table. The spatial resolution depends on the physical capabilities of the scanning table which can be up to 8 dots/mm. Obviously, a noticeable drawback of the technique is the long measurement time which reported to be up to nine hours for a 1×1 m painting (Bonifazzi, et al., 2007). In another research, the spectrophotometer was replaced by a monochromator and a CCD array for a spectral line scan instead of point measurements to enhance the acquisition speed (Antonioli, et al., 2004). Illumination uniformity and lens geometrical distortions are factors to be taken into account prior to measurement in this method.

The applicability of any multispectral imaging system is impacted by several factors but in general, the applicability of any multispectral imaging system for museums is determined by three main factors: cost, speed and accuracy. A reasonable imaging system must provide a balance of all three in capturing components, processing time and data storage requirements. The colorimetric accuracy of the spectral images, as well as their compatibility with common photo-editing software packages, are further empirical requirements (Taplin, and Berns, 2005).

It should be noted that other types of analytical techniques are also available as complimentary sources of material diagnoses. A variety of different types of techniques, including X-ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Optical Microscopy, Raman Spectroscopy and Computed Tomography (CT), provide further data that are applicable in evaluating and validating spectral data and should not be neglected in practical

2.3 Multispectral Capturing Systems for Paintings

Spectroscopy has become a popular and practical method for analyzing works of art in museums. The growth of acquisition technologies in the past decade accelerated the development of affordable acquisition systems to obtain a full spectral image, as opposed to a few spot measurements, with reasonable accuracy becoming of immediate interest, particularly in terms of analyzing, documenting, inpainting, and reproducing artworks in museums (Martinez, et al., 2002; Barni, et al., 2005; Berns, 2005; Cappellini, and Piva, 2006; Fischer, and Kakoulli, 2006; MacDonald, 2006; Bianco, et al., 2011; Berrie, 2012). As already explained, spectral imaging is considered a preferred choice for museums because of the non-invasive nature of the measurements and exclusive advantages for visualization, treatment, reproduction and dissemination procedures. Pigment identification is an off-the-shelf application of spectral data as an aid for painting conservation (Baronti, et al., 1998; Berns, and Imai, 2002; Berns, et al., 2002; Bruni, et al., 2002; Liang, et al., 2008; Zhao, 2008; Ricciardi, et al., 2009; Delaney, et al., 2013).

The visual Arts: Systems for Archiving and Retrieval of Images (VASARI) was the first official project supported in the late 1980s by the National Gallery in London, together with a consortium of European universities, institutions and companies, for capturing digital images of artwork, with the aim of evaluating possible changes in paintings on display or during transportation between museums, as well as documentation and archiving. The capturing system comprised a monochrome digital camera, which moved parallel to the vertical painting using a scanning table, and moving the camera and lighting system to achieve a high-resolution image. Each small section of the painting was captured with several light sources and the final high-resolution image was obtained by merging all small pieces. The final images were up to 20,000 × 20,000 pixels. The color information was calculated using an active illumination system by rotating seven optical broadband filters in front of the
light source. The color conversions were based on a MacBeth ColorChecker (with 24 patches) after flat fielding and corrections for optical scattering of the illumination. The raw output of the VASARI was a high-resolution image for calculating an accurate colorimetric reproduction. The average color difference of VASARI was about 1.1 $\Delta E_{ab}^*$ using a 12-bit monochrome camera. However, one important drawback of VASARI was registration and superposition processes of the captured images, which usually included complex geometric distortions of different part of the paintings (Martinez, et al., 2002; MacDonald, 2006). Despite the multi-channel nature of the system, VASARI cannot be counted as a multispectral imaging system effectively because the spectral data were merely used for accurate colorimetric reproductions. Therefore, the output results are not applicable in material recognition, addressing metamerism or simulating processes such as varnish removal or virtual restorations (Fischer, and Kakoulli, 2006). Two versions of VASARI from 1992 and 2000 are shown in Figure 2.2.

![Figure 2.2: VASARI in years 1997 (left) and 2000 (right) (Martinez, et al., 2002).](image)

The VASARI project was followed by the Methodology for Art Reproduction in Color (MARC) project in mid-1990s with the goal of making high-resolution colorimetric copies of images. MARC II is another enhancement of MARC expediting the capturing speed to a couple of minutes. This project has been used by the National Gallery in London for digital documentation of its entire collection. Similarly, MARC
is limited to colorimetric measurements and reproductions without any multispectral capabilities (Martinez, et al., 2002; MacDonald, 2006).

CRISATEL was the next generation of multispectral imaging systems developed as a successor to VASARI, with the ability to produce digital images with a size of 12,000 × 20,000 pixels and image paintings up to 2×2 meters. The data were acquired by horizontally displacing a CCD composed of a vertically mounted 12,000 pixel linear array. It was equipped with 13 narrow-band interference filters for a better estimation of spectral reflectance in visible and infrared regions of light. Ten narrow-band filters with 40 nm bandwidths subsampled the visible spectrum distributed equally from 380 to 780 nm. Three extra filters with 100 nm bandwidth (i.e. 800, 900 and 1000 nm) captured the reflected light in the infrared region. Two elliptical projectors, positioned on both sides and perpendicular to the painting surface, illuminated the scene. The image capturing time for a 1×1 painting was reported as 20 minutes with a 20 pixels/mm spatial resolution. The color and spectral reproduction accuracy of the system were evaluated by imaging three different color targets. The average color difference between the estimation and reference data were reported from 1.2 to 1.9 CIEDE2000 for different validation color targets (Liang, et al., 2005; Ribés, et al., 2005; Cotte, and Dupraz, 2006; MacDonald, 2006).

One scanning-based spectrophotometric imaging system for paintings developed in Italy was comprised of a scanning table, a monochrome CCD and a spectrograph (Antonioli, et al., 2004; Novati, et al., 2005; Brusco, et al., 2006; Paviotti, et al., 2009). This system, which is a line-scanning imaging system, captured an image of each strip of the painting with spectral resolution of ~2 nm (covering wavelengths from 400 to 700nm) and spatial resolution of about 3.5 lines/mm. The capturing unit had the capacity to scan a total area of 120 × 140 cm² in about three hours. In order to have a complete spectral image further mosaicing processes were necessary. The
color accuracy of the imaging system was evaluated using a set of 14 color glossy standard tiles with the mean \( \Delta E^*_{94} \) of 0.49.

Another multi-spectral scanning system was developed at the University of Ferrara (Carcagni, et al., 2005). This system was composed of 32, 10-nm band interference filters mounted in front of a monochrome CCD camera. The painting’s surface was scanned using an x-y scanning table with a resolution of about 4 dots/mm. At a typical rate of measurement, the acquisition time for a 1 m\(^2\) painting was about nine hours. The color accuracy of the capturing system was assessed by comparing spectral curves of seven standard NPL matte tiles with an average of 1.9 \( \Delta E^*_{ab} \).

The Munsell Color Science Laboratory (MCSL) at the Rochester Institute of Technology (RIT) is another active center for developing spectral acquisition systems. Three multispectral capturing systems with narrow-band color filters, liquid crystal tunable filter (LCTF) and dual-filtered RGB imaging systems have been developed and evaluated (Imai, et al., 2001). The LCTF capturing system gathered the multispectral data by employing a monochrome CCD camera in 31 bands (Imai, et al., 2002; Hensley, and Wyble, 2012). The filtered RGB system as based on a set of RGB values of a trichromatic camera, combined with two filters with optimum transmission curves (Imai, et al., 2003; Berns, et al., 2004; Berns, et al., 2005a). The optimum number and shapes of the filters were selected from a list of commercially available filters with the goal of the maintaining a significant percentage of spectral information (Berns, et al., 2005a). The development of the MCSL spectral framework was followed by the implementation of mathematical techniques for preserving the colorimetric accuracy of spectral images, such as Matrix-R-based and \( Labpqr \) spectral reconstruction methods (Berns, et al., 2005b; Zhao, et al., 2005b; Derhak, and Rosen, 2006; Zhao, and Berns, 2007).

Recently, a remote spectral imaging system, developed by Liang, et al. (Liang, 2012), exploiting a telescope for scanning the wall paintings referred to as the Portable Remote Imaging System for Multispectral Scanning (PRISMS). The spectral imaging
system was capable of measuring visible/NIR (400-800 nm), as well as shortwave infrared (900-1700 nm) by the means of 10 band pass filters (for VIS-NIR) and AOTF (for SWIR) filters. Each band-pass filter had a bandwidth of 40 nm (except for a bandwidth of 70 nm at 880 nm) and were placed within an automated filter wheel. An AOTF was used for spectral acquisition in the IR region with a bandwidth of 10 nm controlled by a computer.

Progressive research has also been carried out by others. For instance, ENST is another center investigating the efficiency of multispectral acquisition systems for image-based spectral estimations studying different sorts of spectral capturing systems and reconstruction methods (Schmitt, et al., 1999; Hardeberg, et al., 2000; Hardeberg, 2001b; Hardeberg, 2001a). The imaging system developed by Tominaga, et al. at Chiba University, captured spectral images by varying the light source and a monochrome camera to boost the measurement speed and remove registration issues. The light source was modulated by a filter wheel or a tunable light source (Tominaga, et al., 2004; Tominaga, 2005; Tominaga, 2012). More inclusive and historical overview of the development of multispectral imaging systems and equipment can be found in Refs. (Martinez, et al., 2002; Fischer, and Kakoulli, 2006; MacDonald, 2006; Tominaga, 2012).

2.4 Spectral Reconstruction

Spectral reconstruction or spectral recovery refers to the methods by which the spectral reflectance of the object is estimated using the output responses of an acquisition system. This is an essential step especially for wide-band multispectral capturing units. Most of the algorithms are based on a linear optical model and additive independent noise (Schmitt, et al., 1999; Haneishi, et al., 2000; Hardeberg, 2001a; Ribes, et al., 2008; Ribes, and Schmitt, 2008). An illustration of a linear optical model including multiple filters and illuminants is shown in Figure 2.3.
Figure 2.3: A schematic view of an imaging system.

The acquisition responses are the integration of the light energy that reaches the sensor, weighted by the total sensitivity of the channels. Following this definition, the output response of each channel \((S_{R,K})\) for \(K\)-th filter \((\varphi_K)\) and \(R\)-th illuminant \((I_R)\) at 2-D coordinate \(x\) can be expressed as:

\[
S_{R,K}(x) = \int_{\lambda_1}^{\lambda_2} I_R(\lambda, x) \rho(\lambda, x) o(\lambda, x) \varphi_K(\lambda, x) a(\lambda, x) d\lambda + e_1(x), \tag{2.1}
\]

where \(a\) is the detector sensitivity, \(\varphi\) is the filter transmission, \(o\) is the interaction of the optical path, \(\rho\) is the spectral reflectance and \(e\) is additive noise. \(\lambda_1\) and \(\lambda_2\) determine the range of light wavelength depending on the sensitivity of the detector, filters and illuminants. The channel sensitivity can be defined as the result of filter transmission, the sensitivity of the detector, illuminants and the effect of the optical path:

\[
C_{R,K}(x) = I_R(\lambda, x) o(\lambda, x) \varphi_K(\lambda, x) a(\lambda, x) \tag{2.2}
\]
The formulation can be written in discrete form at $N$ different wavelengths, $\lambda_j$, and wavelength sampling interval $\Delta \lambda$:

$$S_{R,K}(x) = \sum_{j=1}^{N} \rho(\lambda_j, x) C_{R,K}(\lambda_j, x) \Delta \lambda + e_i(x)$$  \hspace{1cm} \text{Eq. 2.3}

The matrix representation of the same equation is as follows:

$$S = \rho C + E$$  \hspace{1cm} \text{Eq. 2.4}

where:

$$S = [S_{R,K}(x)],$$  \hspace{1cm} \text{Eq. 2.5}

$$C = [C_{R,K}(\lambda_j, x)],$$  \hspace{1cm} \text{Eq. 2.6}

$$\rho = [\rho(\lambda_j, x)]$$  \hspace{1cm} \text{Eq. 2.7}

Spectral reconstruction algorithms transform the captured signals, $S$, to an estimation for vector $\rho$ in Eq. 2.4. However, the estimation of the spectral reflectance is difficult because vector $S$ is the result of the integration of spectral reflectance over vectors in matrix $C$ with fewer numbers of elements compared to the dimensionality of spectral reflectance curves. Mathematically, this is an ill-posed problem in which the solution for $\rho$ is not unique (Ribes, and Schmitt, 2008). An estimation of $\rho$ can be attained using the pseudo-inverse of matrix $C$ and neglecting the noise element. Matrix $C$ itself can be estimated by characterizing the components of the imaging system of the Figure 2.3 and Eq. 2.2. In this method all the components are characterized independently and directly, also referred to as direct measurement of the matrix $C$. This technique, however, requires specific laboratory facilities and measurement conditions to create and measure a standard monochromatic light, which is not always accessible. Moreover, the pseudo-inverse of matrix $C$ may not result in a stable solution making it extremely sensitive to small errors. A second alternative is to estimate the pseudo-inverse matrix using a set of training targets also referred to as learning-based or target-based reconstruction.
methods (Hardeberg, 2001a; ISO, 2006; Ribes, et al., 2008). In the target-based characterization method, this relationship is established according to a set of color patches with available, pre-measured spectral or colorimetric data. Target-based characterization methods are inexpensive and more practical compared to the other methods. A variety of statistical and numerical techniques can be applied according to the noise level, technical characteristics of the capturing unit and the nature of the specimen being examined that have been discussed and available in the literature (Hardeberg, 2001a; Fairman, and Brill, 2004; Berns, 2005; Keenan, 2007; Nyström, 2007; Zhao, and Berns, 2007; Ribes, et al., 2008; Ribes, and Schmitt, 2008; Moghareh Abed, et al., 2009; Bianco, et al., 2011; Tominaga, 2012; Peyvandi, et al., 2013, Burns and Berns, 1996; Connah, et al. 2004, Finlayson, and Drew 1997).

2.5 Spectral Calibration and characterization

The term calibration is defined as maintaining the device with a fixed known output response pre-determined for characterization. Characterization is the process of connecting device-dependent and device-independent color spaces for a calibrated device (Sharma, 2003). Besides the capacities of image-capturing hardware, color characterization and calibration techniques can be a significant source of error in the acquisition steps. It is also important to have a reliable system so that it follows the optical model explained in Eq. 2.1. Any deviations from the model can cause errors cascading throughout the whole system.

For digital still cameras (DSCs), color characterization methods refer to the technique of transforming camera responses (e.g. RGB) to a device-independent colorimetric representation (e.g. CIEXYZ) (Green, and MacDonald, 2002; Sharma, 2003; Westland, et al., 2004; Fairchild, 2005). In spectral imaging, the spectral characterization process refers to the procedure to convert the multispectral camera responses (device-dependent space) to spectral reflectance with known capturing geometry (device-independent space), which also includes spectral reconstruction algorithms.
Calibrating a multispectral acquisition system is quite similar to regular digital cameras in many aspects (Lopez-Alvarez, et al., 2009; Liang, 2012). The linearity of the detector, noise characterization, dark current and flat fielding are some of the regular steps in calibrating digital trichromatic cameras. However, extra procedures might be needed associated with the spectral properties of the capturing systems such as the transmittance shift of the LCTF with incident angles reported by some authors (Baronti, et al., 1998; Liang, et al., 2005; Ribés, et al., 2005). The calibration process has a considerable impact on the target-based methods where the parameters of the model are derived according to a set of standard samples. The target-based color characterization of DSCs has been the subject of many research papers in the past decade (Hong, et al., 2001; Barnard, and Funt, 2002; Li, et al., 2003; Martínez Verdú, et al., 2003; Cheung, and Westland, 2004; Cheung, et al., 2004a; Cheung, et al., 2004b; Nyström, 2007; Fairchild, et al., 2008), evaluating a number of factors affecting the accuracy of color characterization regarding utilized characterization algorithms, color target structure and camera hardware. The conclusions mostly point out that target-based characterization methods are valid for a particular lighting geometry, color target materials and surface structure. This dependency had led to designing optimized color targets in recent research, taking into account several factors, such as material, gamut and the number of color patches, with less consideration for the role of lighting geometry on the color target appearance. The variety of capturing geometries and the uncontrolled nature thereof are other factors increasing the complexity of the characterization process. The more divergent these geometries and the differences in surface properties between the profiling target and object, the greater the characterization error. To avoid possible appearance changes caused by the capturing geometries, it is recommended to keep the viewing/illuminating geometry consistent with the measurement geometry and typical observing conditions (Hong, et al., 2001; Green, and MacDonald, 2002; Sharma, 2003). The material aspects become problematic particularly when color patches vary in surface and spectral properties, leading to different appearance changes according to geometry changes.
2.6 Pigment Identification Using Spectral Data

Pigment identification is a distinct application of spectral imaging. This applicability has been studied by a handful of researchers in the past decade (Berns, and Imai, 2002; Berns, et al., 2002; Delaney, et al., 2005; Liang, et al., 2008; Zhao, 2008; Ricciardi, et al., 2009; Toque, et al., 2010; Delaney, et al., 2013). The choice of spectral-based pigment identification pipeline is affected by many other factors such as equipment, specimen and other practical preferences.

The research by Baronti, et al. (Baronti, et al., 1998) is one of the earliest attempts for deriving pigment information from visible spectral images of paintings. A multispectral capturing system with 29 narrowband filters in VIS and NIR was set up for spectral imaging. The idea was to use PCA for spectral analysis of the spectral image and find a correlation to the pigment information. The pigment identification was carried out by analyzing the 2-D plane of the PCA coefficients vs. reflectance data at certain wavelengths. The proposed workflow was trained and evaluated by a limited number of known pigments. The preliminary results expanded to the spectral data of an oil-painted panel by Luca Signorelli. However, no definite conclusions made about the possibility of certain pigments with the painting under examination. Cluster analysis of the 2D histograms of PCA coefficients and the reflectance values at particular wavelengths also were suggested by the author for possible further analysis.

The use of spectral imagery and statistical analysis for pigment identification has been investigated by other researchers. The research by Delaney, et al. (Delaney, et al., 2005; Ricciardi, et al., 2009; Delaney, et al., 2013) involves a combination of analytical methods along with the spectral imagery for material diagnosis. In this study, spectral imaging was used for discriminating different blue pigments in two paintings by Vincent van Gogh from the collection of the National Gallery of Art, Washington, D.C. The spectral image was collected using a CCD camera fitted with eight band-pass filters in the visible, near infrared and short wavelength spectral
regions. The spectral data were constructed and analyzed in the spectral reflectance space using ENVI software. ENVI is a popular software for the analysis and visualization of scientific data and imagery used in a variety of industries, including remote sensing, engineering, geology, aerospace, defense and intelligence, and medical imaging. The conclusions revealed the ability of spectral imaging, as a non-invasive and in-situ method in recognizing the blue pigments and specifying regions of high concentration.

Ricciardi, et al (Ricciardi, et al., 2009) also combined XRF and Raman spectroscopy analysis with multispectral imaging and FORS in visible and NIR ranges for extracting pigment information and pigment distribution maps. The multispectral system comprised a four-megapixel CCD camera and a filter wheel with 12 band-pass interference filters covering the spectral range of 400 to 950 nm in 50 nm steps. The spectral image was analyzed in ENVI to extract 12 endmembers associated with the results from XRF and FORS. Finally, an approximation of proportion maps was used to specify the concentration of different endmembers or primaries.

In similar research by Delaney, et al. (Delaney, et al., 2013), the same low-resolution 12-band multispectral camera system, operating from 400 to 950 nm was used to obtain spectral images. A Pixel Purity Index (PPI) based endmember detection algorithm (Boardman, et al., 1995; Chang, and Plaza, 2006), embedded in ENVI software, was used for pigment identification in a spectral reflectance-based space. The Maximum Noise Fraction (MNF) method was used for reducing the spectral reflectance dimensionality to 12 possible eigenimages with meaningful information. Eventually, a clustering algorithm was applied for manually selecting well-separated endmembers. The extracted endmembers were compared to the results of other analytical methods (such as FORS, XRF or Raman spectroscopy) for final evaluations. The endmembers were correlated to a pre-existing list of pigments, obtained by XRF and FORS, using a spectral angle-mapping (SAM) index. The endmembers were used to create concentrations maps as representative of the proportions of the endmembers for each pixel.
In the mentioned research, analytical unmixing algorithms are directly applied to the acquired spectral data for pigment identifications. Leaving aside the accuracy of the spectral capturing unit, the analysis of the pigment identification and concentration is not effectively valid since the subtractive mixtures are non-linear in the spectral reflectance space. This uncertainty necessitates a combination of other sources of material indication methods (such as XRF and FORS) for more definite predictions.

Berns and Imai (Berns, and Imai, 2002) and Berns, et al. (Berns, et al., 2002) at MCSL investigated the application of spectral information for pigment identification and pigment selection for inpainting, but in a subtractive mixing space. Berns and Imai (Berns, and Imai, 2002) developed a six-channel multispectral acquisition system for spectral sampling. The camera responses were gathered using a trichromatic camera with and without a light blue filter. The camera signals were then used as an input for a spectral estimation algorithm according to a training target made of 68 modern artist oil paints and titanium white. Estimated spectral reflectances were converted to (K/S) subtractive mixing space for further pigment evaluations. The pigment information was extracted according to the RMS errors of the (K/S) curves of estimated and a pre-existing pigment database. The conclusion implied that the accuracy of spectral estimation has a considerable influence on the performance of the pigment identification.

The research at MCSL was followed by further subtractive mixing analysis, high-resolution spectral capturing (Zhao, et al., 2005a; Zhao, et al., 2005b; Zhao, and Berns, 2007), pigment identification and pigment mapping (Zhao, et al., 2006; Zhao, 2008; Zhao, et al., 2008). The goal was to develop a practical paradigm for spectral measurement and pigment analysis specifically for museums. Mohammadi and Berns (Mohammadi, and Berns, 2004), Zhao, and Berns (Zhao, and Berns, 2009) and Berns, and Mohammadi (Berns, and Mohammadi, 2007) evaluated the validity of the KM-based models for characterizing paint layers. The results were used for pigment
identification and concentration estimations by Zhao (Zhao, 2008), Zhao, et al. (Zhao, et al., 2006) and Zhao, et al. (Zhao, et al., 2008).

Zhao, et al. (Zhao, et al., 2006) employed a multi-channel acquisition system for spectral estimations. The spectral image was classified in five subsections using the k-Means segmentation algorithm based on an Euclidian distance metric in the CIELAB color space. Each section was assessed for pigment identification independently, using a pre-existing pigment database. The candidate pigments in each section were selected according to the assumption of the existence of pure pigment. Each pure element was compared to the database using a search procedure. Knowing the primary pigments, two-Constant KM theory was used for improving estimated spectral estimation of multi-channel capturing system and to compile the concentration maps (Zhao, et al., 2005a).

In the research by Zhao, et al. (Zhao, et al., 2008), a more sophisticated pipeline was designed to analyze The Starry Night, painted by Vincent van Gogh in 1889. A high-resolution (22 megapixels) six-channel Sinarback 54 camera with two optimized filters at 45°:0 geometry was used for the multispectral measurements. The spectral reflectance curves were estimated using a ColorChecker DC and the Matrix-R method (Zhao, and Berns, 2007). The spectral image was then segmented into smaller pieces to facilitate the calculation and shorten the processing time. Each segment itself was classified into smaller segments using a supervised classification algorithm by a Euclidean distance function in six-channel camera space. The single-constant KM theory was applied for pigment identification and concentration estimations within each cluster, taking the pigment database into consideration. The choice of the single-constant KM theory over the original two-constant KM theory was its shorter processing time and its inexpensive calculations, even though the author recommended the two-constant KM for more accurate predictions. Pigment concentrations were calculated for a limited number of selected pixels in each cluster to improve the algorithm speed. Other than technical limitation of the method, it was pointed out that more investigation of spectral measurement and
pigment identification were still required for more precise predictions, particularly for dark mixtures and masstones (Berns, et al., 2008).

In another recent study, Liang, et al. (Liang, et al., 2008) utilized spectral data and the single-constant KM theory for pigment identification purposes, using a simple cross-correlation method to compare the K/S curves of pure pigments to a pre-existing pigment database. First, she mentioned the influence of particle size, binding medium and concentration of spectral properties of the mixtures. The author also discussed the peak wavelength shift of dark mixtures due to changes in particle size and concentration. The single-constant KM theory was applied for pigment identification by comparing the unknown spectrum to combinations of a known pigment database. The combination set with the maximum correlation values was chosen as the final primary set. Eventually, the data from a multispectral capturing system, PRISM (Liang, et al., 2005; Liang, 2012), was combined with Fourier domain optical coherence tomography (OCT) for final pigment identification for a limited number of pixels.

Past research indicates several factors to promote pigment identification estimations: first, utilizing accurate and more precise spectral data rather than reconstructed spectral reflectances so that the effect of any mixing theory can be assessed regardless of spectral accuracy; second, implementation and evaluation of a reasonable subtractive mixing model, e.g. KM theory for pigment identification; and finally, applicability of any proposed method for high-resolution images.

### 2.7 Spectral Unmixing in Remote Sensing

Spectral unmixing refers to the procedures by which the measured spectrum of a mixed pixel is decomposed into a collection of spectral primaries, called endmembers. The procedure also includes estimating the proportion (or fractional abundances) of each of the endmembers present in a given pixel. Similar to pigment identification methods, endmembers in remote sensing and GIS generally
correspond to familiar materials, such as different kinds of soil, water, metal, vegetation, etc. (Keshava, 2003).

Most of the available unmixing algorithms are based on a linear mixing model (LMM). In a LMM, it is assumed that the reflected radiation for each pixel is the linear combination of the endmembers with the same fractional abundances as the area coverage of each endmember (Figure 2.4). The LMM is subject to two constraints for the abundances to be non-negative and have full additivity (including the summation to one).

![Figure 2.4: An illustration of the additive linear mixing for a pixel measured by the sensor (Keshava, and Mustard, 2002; Keshava, 2003).](image)

In a linear additive mixing model, the spectral curve for the $i$-th pixel of the image, $X_i$, is modeled as follows:

$$X_i = \sum_{k=1}^{M} p_{ik} E_k + n_i, i = 1, ..., N,$$

Eq. 2.8
where $E_k$ represents the vector of the $k$-th endmember and $p_{ik}$ is the proportion of the corresponding endmember for the $i$-th pixel. $M$ and $N$ are the number of endmembers and image pixels respectively; $n_i$ is the measurement noise for $i$-th pixel. The proportion values, $p$, are subject to the convexity and positivity:

$$\sum_{k=1}^{M} p_{ik} = 1, p_{ik} \geq 0$$  \hspace{1cm} \text{Eq. 2.9}$$

Even though the linearity assumption is inconstant in nature, LMM is the most frequently used model for representing the syntheses of mixed pixels from distinct endmembers owing to its due to tractability and simplicity (Keshava, and Mustard, 2002; Keshava, 2003).

### 2.7.1 Dimensionality Reduction

Most of the unmixing algorithms are applied in a subspace of the actual spectral space before further analysis is undertaken. Theoretically, the actual dimensionality linearly mixed data are equivalent to the number of endmembers. Consequently, the variation of the data is fully characterized in a lower dimensional space without los of information. Applying the unmixing algorithms on the representative of the spectral data, but in lower dimension, expedites the calculation and simplifies the process. However, it is also valid to apply the unmixing algorithms to the actual high-dimensional space mathematically.

Two popular dimension reduction algorithms are principal component analysis (PCA) and MNF or noise adjusted PCA (NAPCA). PCA is a well-known statistical approach that decomposes N-dimensional data to a set of orthonormal eigenvector. Due to the mathematical preferences, the decomposition is applied on the covariance matrix of data, $\Sigma$:

$$\Sigma = \frac{1}{N} \sum_{k=1}^{N} (X_i - \mu)(X_i - \mu)^T$$  \hspace{1cm} \text{Eq. 2.10}$$
Where $\mu$ is vector of the mean of all the pixels, $X_i$. PCA decomposes the covariance matrix to a set of orthonormal basis functions as follows:

$$\mathbf{\Lambda} = \mathbf{U}\mathbf{\Sigma}\mathbf{U}^T$$  \hspace{1cm} \text{Eq. 2.11}

In this equation, $\mathbf{U}$ is the matrix of orthonormal basis functions or eigenvectors and $\mathbf{\Lambda}$ is a diagonal matrix of eigenvalues. The magnitudes of the eigenvalues indicate the variation of the data corresponding to each of the eigenvectors. Orthonormal eigenvectors span the same space as the data, thus the data can be expressed by the new coordinates of the orthonormal basis vectors, $c_i$:

$$X_i - \mu = \mathbf{U}c_i$$  \hspace{1cm} \text{Eq. 2.12}

$$c_i = \mathbf{U}^T(X_i - \mu)$$  \hspace{1cm} \text{Eq. 2.13}

If all of the columns of matrix $\mathbf{U}$ are used for calculation, the transformation is a rotation in the same dimensional space as $X_i$. However, for dimensionality reduction, only eigenvectors of $\mathbf{U}$ correspond to the total variability of a certain threshold are kept. The remained residuals are usually small and ascribed to noise.

The MNF is similar to PCA but the noise variation is adjusted to one in order to maximize the SNR instead of the data variance. Consequently, an estimation of the noise covariance matrix is required. Covariance of uncorrelated noise, $\Sigma_n$, can be either measure from direct measurements, e.g. using a flat-field image, or estimated using the spectral image itself. The MNF transforms the data to a new space, noise whitened space, so that the noise variance equals unity for all bands. Afterward, the regular PCA is applied to the noise-whitened data. The MNF primaries can be expressed as follows (Green, et al., 1988; Lee, et al., 1990; Xu, and Gong, 2008):

$$\mathbf{\Lambda}_n = \mathbf{U}_n\Sigma_n\mathbf{U}_n^T$$  \hspace{1cm} \text{Eq. 2.14}

where $\mathbf{\Lambda}_n$ and $\mathbf{U}_n$ are eigenvalues and eigenvectors yielded from the covariance matrix of noise image. The eigenvalues of noise can be forced to be one using a set of orthogonal (but not normal) eigenvectors:
I = \Lambda_n^{-\frac{1}{2}} U_n \Sigma_n U_n^T \Lambda_n^{-\frac{1}{2}} \quad \text{Eq. 2.15}

where I is the identity matrix. By letting

F = \Lambda_n^{-\frac{1}{2}} U_n \quad \text{Eq. 2.16}

the covariance of noise is decomposed so the eigenvalues are one for all of the orthogonal bands:

I = F \Sigma_n F^T \quad \text{Eq. 2.17}

Noise-whitened covariance matrix, \Sigma_{n,adj}, is expressed as follows:

\Sigma_{n,adj} = F \Sigma F^T \quad \text{Eq. 2.18}

Finally eigenvectors of the noise-whitened data are calculated:

\Lambda_{n,adj} = G \Sigma_{n,adj} G^T \quad \text{Eq. 2.19}

In summary, the process of calculating MNF coefficients is summarized as follows:

\[ c_{i,n,adj} = G^T \Lambda_n^{-\frac{1}{2}} U_n^T (X_i - \mu) \quad \text{Eq. 2.20} \]

The estimated values corresponding to the chosen eigenvectors, \( G_i \) is expressed as following equation:

\[ \hat{X_i} = U_n \Lambda_n^{-\frac{1}{2}} G_i (c_{i,n,adj}) + \mu \quad \text{Eq. 2.21} \]

MNF method is recommended over PCA for most of the unmixing procedures. However, difficulties in noise measurements and correlations between spectral bands limit the use of MNF in practice.

2.7.2 Spectral Distance Functions

A spectral distance function, also called a dissimilarity measure, expresses the differences between two spectral curves by a single number. Several spectral
distance functions have been recommended for spectral imaging in the literature [98], four of which are selected due to their popularity, simplicity and robustness of the method.

### 2.7.2.1 L2 Euclidean Distance

This function is the simple L2 distance of two points in an n-dimensional space. The calculation of the L2 distance function is easy and computationally fast. L2 distance function is calculated according to Eq. 2.22:

\[
D_{L2} = \left( \sum_{i=1}^{p} (X_{1i} - X_{2i})^2 \right)^{1/2}
\]

Eq. 2.22

### 2.7.2.2 GMC Euclidean Distance

German-McClure distance function dedicates more sensitivity to small differences. This distance function can be considered as an L2 distance function with a non-linear weighting based on the differences in each band. This distance function is calculated as follows:

\[
D_{GMC} = \sum_{i=1}^{p} \frac{(X_{1i} - X_{2i})^2}{1 + (X_{1i} - X_{2i})^2}
\]

Eq. 2.23

### 2.7.2.3 \( \chi^2 \) Distance Function

This distance function is reported to have a reasonable performance in analyzing multispectral images. \( \chi^2 \) distance function is calculated as follows:

\[
D_{\chi^2} = \sum_{i=1}^{p} \frac{(X_{1i} - X_{2i})^2}{(X_{1i} + X_{2i})^2}
\]

Eq. 2.24

### 2.7.2.4 Angular Distances

These types of spectral distance functions are based on the angle between two spectral vectors, also called spectral angular mapper (SAM). The function can be in
log, arc cosine or other mathematical forms. For this research, the arc cosine version of the distance function was chosen for spectral comparisons:

\[ D_{SAM} = \arccos \left( \sum_{i=1}^{p} \frac{X_{1i} X_{2i}}{|X_1| |X_2|} \right) \]  
Eq. 2.25

### 2.7.2.5 CIEDE2000

This distance function is the CIEDE2000 of two spectral curves for a given viewing condition. An advantage of CIEDE2000 is its perceptual traits that distinguish it from other distance functions. The drawbacks of using this function are the possibility of a metameric match for an alternative light source and complicated calculations. The \( \Delta E^*_{94} \) color-difference formula is used when large numbers of pixels are involved.

### 2.7.3 Endmember Extraction Methods

Once convexity and linearity are assumed, available LMM-based unmixing algorithms become eligible for unmixing purposes. Some of most popular methods include Pixel Purity Index (PPI) (Boardman, et al., 1995; Chang, and Plaza, 2006), Vertex Component Analysis (VCA) (Nascimento, and Dias, 2005b), N-FINDR (Winter, 1999), Iterative Error Analysis (IEA) (Neville, et al., 1999), Optical Real-time Adaptive Spectral Identification System (ORASIS) (Bowles, et al., 1998), Convex Cone Analysis (CCA) (Ifarraguerri, and Chang, 1999; Gruninger, et al., 2003; Gruninger, et al., 2004), Orthogonal Subspace Projection (OSP) (Harsanyi, and Chang, 1994), Iterated Constrained End-member (ICE) (Berman, et al., 2004), Sparsity Promoting Iterated Constrained End-member (SPICE) (Zare, and Gader, 2007), Automatic Morphological End-member Extraction (AMEE) (Plaza, et al., 2002), Spatial Spectral End-member Extraction (SSE), Successive Projection Algorithm (SPA) (Zhang, et al., 2008), Nonnegative Matrix Factorization (NMF) (Miao, and Qi, 2007), Maximum Distance (MaxD) (Schott, et al., 2003), Sequential Maximum Angel Convex Cone (SMACC) (Gruninger, et al., 2004) and Simplex-Based
Methods (Fuhrmann, 1999; Bajorski, 2005; Chang, et al., 2006). In most of the algorithms, a dimensional reduction technique (e.g. PCA, MNF, SVD) is used to reduce the dimensionality of the spectral data and reduce the computational burden (Green, et al., 1988; Lee, et al., 1990; Keenan, 2007; Xu, and Gong, 2008). The unmixing algorithms are mostly based on the geometrical shape of the convex simplex, morphological or spatial characteristics of the captured spectral data (Veganzones, and Grana, 2008; Plaza, et al., 2011). Below is a short summary of the most popular unmixing methods.

2.7.3.1 **Pixel Purity Index (PPI)**

Pixel Purity Index or PPI is one of the most successful and easy to implement approaches for endmember extraction. The algorithm is applied to dimensional reduced data, starting with generating a large number of random vectors, called skewers, with the same dimensionality of the natural data. All the data points are projected onto each of the skewers and the *pixel purity score* is calculated for each point. The *pixel purity score* is the total number of times that the point gains the maximum length after projecting onto the skewers. After many repeated projections, pixels with a larger *pixel purity index* are considered as pure elements. The PPI method does not indicate a perfect estimation of endmembers, but is a proper guide for further analysis. The number of random vectors and the choice of the desired pure pixels are counted as shortcoming of this algorithm. In practice, PPI is considered an intermediate step for most unmixing algorithms (Bowles, et al., 1998; Theiler, et al., 2000; Chang, and Plaza, 2006).

2.7.3.2 **N-Finder**

N-Finder is an automated endmember extraction algorithm that searches the set of pixels of a simplex with maximum volume in a dimension reduction step. The algorithm is based on the existence of pure elements in the spectral image. It starts with at least M number of initial sets of points in a M-1 dimensional subspace. Next, a randomly selected pixel is added to the initial sets. If the new pixel leads to the simplex to have larger volume, the pixel set forming the simplex with maximum
volume is kept. The algorithm continues until there is no replacement of the selected pixels available. Finally, the selected pixels are considered as end-members. This algorithm is sensitive to the choice of the starting data points, noise and number of iterations (Winter, 1999). The volume of the simplex is calculated using the determinant of the matrix shown in Eq. 2.26.

\[
E = \begin{bmatrix}
1 & 1 & \cdots & 1 \\
e_1 & e_2 & \cdots & e_M
\end{bmatrix}_{M \times M}
\]

Eq. 2.26

In this equation \(e_i\) are endmember column vectors and \(M\) is the number of endmembers. The volume of the simplex, \(V\), is proportional to the determinant of the matrix \(E\):

\[
V(E) = \frac{1}{M-1} |\det(E)|
\]

Eq. 2.27

The N-Finder algorithm can be followed by a simulated annealing algorithm (SA) to refine the searching process (Veganzones, and Grana, 2008).

2.7.3.3 Simplex Growing Algorithm (SGA)

SGA (Chang, et al., 2006) is a simplex-based algorithm in which the simplex with the maximum volume is searched sequentially. Usually, the algorithm starts with a single endmember of the maximum length. Thereafter, a new vertex that leads to the simplex with the maximum volume is selected as the new endmember. The same procedure is repeated until the desired number of endmembers is reached. However, the algorithm is analogous to the N-Finder algorithm, but instead of randomizing all the vertices of the simplex simultaneously, one vector at the time is optimized. Since the results are depended on the endmember, algorithm is repeated for a set of randomly selected endmember in the initiation step.

2.7.3.4 Orthogonal Subspace Projection (OSP)

In OSP algorithm (Harsanyi, and Chang, 1994) the pixel vector with maximum lengths is selected as the first endmember. Afterwards, the data are projected onto the space orthogonal to the first selected endmember. The pixel with the largest
length in the projected space is labeled as the second endmember. Next, the spectral data are projected into the hyperplane orthogonal to the first two endmembers and the pixel with the maximum projection is selected as the third endmember. The projection process is repeated until the desired number of endmembers is extracted. The algorithm can be applied to the image with no dimensional reduction. The algorithm is similar to Maximum Distance (MaxD) method presented by Schott, et al. (Schott, et al., 2003) but the first two endmembers are defined by the vectors with and smallest magnitude. The algorithm is based on the fact that the vertices of a ND simplex remain the same for (N-1)D simples after projection to the subspace orthogonal previously chosen endmembers (Lee, 2003).

2.7.3.5 Vertex Component Analysis (VCA)

The VCA algorithm presented in Ref. (Nascimento, and Dias, 2005b) is also based on the concept of successive orthogonal subspace projections. VCA exploits the fact that the affine transformation of a simplex is also a simplex. With the assumption that the endmembers of a set of data are placed on the vertices of the simplex that encloses the data, endmembers are extracted according to successive projection of the hyper simplex to lower dimensions. Unlike OSP, VCA algorithm is followed by growing the simplex through adding the new vertex with the maximum length in the null space of previous endmember. The data are successively projected to the null space of previously selected endmembers until sufficient number of endmember is indicated.

2.7.3.6 Iterative Error Analysis (IEA)

IEA (Neville, et al., 1999) is an iterative method in which the endmembers are estimated by minimizing the root sum squares (RSS) of the residuals associated with a set of already chosen endmembers:

$$RSS = \sum_{i=1}^{N} \left( X_i - \sum_{j=k}^{M} p_{ik} E_k \right)^2$$

Eq. 2.28
The calculations are subject to convexity and positivity of abundances (Eq. 2.9). In each iteration, a set of points that causes the maximum estimation error is averaged to produce the new sets of candidates of endmembers.

2.7.3.7 Iterated Constrained End-member (ICE)

Berman, et. al. (Berman, et al., 2004) implemented ICE algorithms to perform a minimization of the regularized residual sum of squares shown in Eq. 2.28 according to a set of constraints. The regularization term is the volume of the simplex made by the endmembers. It has been shown that the Euclidian distance of the endmembers is a proper representation of the absolute volume of the simplex, SSD, with a shorter processing time. Berman, et. al. provided a simpler formulation that substituted the volume based on the sum of Euclidean distance of the endmembers Eq. 2.29.

$$SSD = \sum_{k=1}^{M-1} \sum_{i=2}^{M} (E_k - E_i)^2 = M(M - 1)V \quad \text{Eq. 2.29}$$

where $V$ is the sum of variances (over the bands) of the simplex endmembers. A non-linear algorithm optimizes the endmembers in order to minimize the objective function in the iterations. The objective function can be written as follows:

$$RSS_{Reg} = \frac{(1 - \mu)RSS}{N} + \mu SSD \quad \text{Eq. 2.30}$$

where $\mu$, the regularization parameter, should be set between zero and unity. Suggested values for $\mu$ are 0.05 or 0.1 according to the dataset. The optimization is based on a known number of endmembers, initial values and after dimensional reduction step. The starting points can be based on primitive endmember selection methods such as N-Finder or PPI.

2.7.3.8 Sparsity Promoting Iterated Constrained End-member (SPICE)

SPICE is a later version of ICE by Zare, and Gader (Zare, and Gader, 2007; Zare, 2008), and is based on the same non-linear optimization algorithm and regularization terms. However, a new sparsity term is added to the objective function. Similar to ICE, this method is applied after dimension reduction and based
on the initial points. The sparsity term controls the proportions or abundances in order to have sparse values in the optimization loop. Accordingly, the endmembers that have a tighter fit to the data set are extracted. The sparsity regularization term is defined as follows:

\[ SPT = \sum_{i=1}^{N} \gamma_k \sum_{k=1}^{M} |p_{ik}| \]  

Eq. 2.31

\[ \gamma_k = \frac{\Gamma}{\sum_{i=1}^{N} p_{ik}} \]  

Eq. 2.32

The non-linear optimization loop minimizes to objective function iteratively, expressed in Eq. 2.33.

\[ RSS_{Reg}^* = \frac{(1-\mu)RSS}{N} + \mu SSD + SPT \]  

Eq. 2.33

\( \Gamma \) defines the contribution of the sparsity term to the minimization process recommended to set to 5, 10 or 20.

2.7.3.9 Convex Cone Analysis (CCA)

In this method, a linear combination of E number of eigenvectors corresponds to the largest eigenvalues of PCA or MNF dimension reduction step. The total number of endmember, E, must be already known in advance. The method is based on non-negativity of endmembers (Ifarraguierri, and Chang, 1999; Gruninger, et al., 2003; Gruninger, et al., 2004) as a linear combination of the maintained eigenvectors. The linear combination of E eigenvectors is written as follows:

\[ h = p_1 + a_1p_2 + \cdots + a_{E-1}p_E \]  

Eq. 2.34

where \( p_i \) are N×1 eigenvectors corresponding to the largest eigenvalues and N is the dimensionality of the spectral data. The convex cones are calculated by setting the equation to zero vector (\( \theta \)):

\[ \theta = p_1 + a_1p_2 + \cdots + a_{E-1}p_E \]  

Eq. 2.35
Since N is greater than E the equation system is an over-determined system. However, the equation system has exact solution when E-1 number of bands is selected. In the implementation of the CCA method, all combination bands of \( \binom{N}{E-1} \) are used to for solution of the Eq. 2.35. Calculated coefficients are plugged back to Eq. 2.35 when all the bands are involved. The linear solution will result in at least E-1 zeros and other values for reminding bands. The combination set with all positive values for all the bands is selected as The final endmembers. Even though the method results in all positive endmembers, it does not provide endmembers that tightly surround the data points.

2.7.3.10 Automatic Morphological End-member Extraction (AMEE)

AMME (Plaza, et al., 2002) is a mathematical, morphology-inspired algorithm that uses spatial information for the process of extracting spectral endmembers. The algorithm is based on the definition of multispectral erosion and dilation operators and should be applied to the original spectral data. Multichannel erosion operator indicates pixels with more similarity to the neighbors as opposed to multichannel dilation that specifies pixels with the most spectral difference to the neighbors. The morphological images are influenced by the kernel size, also called structuring element (SE), as a prior parameter for erosion and dilation operators. The SE controls extracting or neglecting the features of the image contents, according to its size and shape. The operators applied to the images for variety of kernel size to form the Morphological Eccentricity Index (MEI) image to be used for endmember selections. The final endmembers are specified after a fully-automated approach that consists of an automated segmentation of the MEI image followed by spatial/spectral region selection and a growing-based clustering algorithm.

2.7.3.11 Other Unmixing Methods

Mathematical aspects of unmixing problems enable the application of a wide variety of algorithms and theories to address the problem. Non-negative Matrix Factorization (NMF) is another unmixing algorithm presented in Ref. (Miao, and Qi, 2007) where an iterative matrix factorization method is constructed according to
the non-negativity and summation to one constraints along with the minimization of the volume of the simplex enclosing the data. The algorithm is rather analogous to ICE but substitutes the RSS with the NMF criteria.

The MNF is recommended as the dimension reduction step prior to the unmixing algorithm; however it can be replaced by other available choices such as independent component analysis (ICA) (Bayliss, et al., 1998; Nascimento, and Dias, 2005a), which affect results according to the nature of the spectral data and the endmembers. There are other methods available when non-linear mixing is involved such as artificial neural network (ANN) (Foody, et al., 1997) and adaptive kernel-based technique (Broadwater, and Banerjee, 2011). More comprehensive explanations and comparisons of different methods can be found in Refs. (Keshava, and Mustard, 2002; Keshava, 2003; Martínez, et al., 2006; Veganzones, and Grana, 2008; Plaza, et al., 2011; Bioucas-Dias, et al., 2012; Chang, 2013).

2.7.4 Intrinsic Dimension Estimation

Estimating the intrinsic dimension (ID) or the number of endmembers is a challenging part of an unmixing paradigm. The ID is defined as the dimension, \( M \), of the subspace spanning the signal space apart from noise. Since noise has as many dimensions as the existing bands, the dimensionality of the raw data is higher than its actual intrinsic value. Accordingly, Determining ID is the initial step of separating the signal from the noise, which is an ongoing area of research (Cawse-Nicholson, 2013; Chang, 2013).

The ID estimation methods can be classified into two categories. The first is methods that require an estimation of noise for the estimation. Unfortunately, the estimation of noise behavior based on the captured spectral image is a difficult task. For instance, noise properties can be estimated using a uniform noise image or according to other mathematical characteristics of the spectral image. In most cases, it is also assumed that the noise is independent and identically distributed for
simplification. Covariance matrix of the observations, Eq. 2.10, is also used in the majority of the techniques in this category, which can be calculated from the image easily. The second is geometric algorithms that are independent of noise estimations. These class of methods evaluate the characteristics of the simplex for ID determination. Both cases are usually accomplished based on a set of thresholds, adjusted manually by the operator.

In this section, five state-of-the-art methods of ID determinations were explained briefly. More references of the ID estimation for spectral imagery can be found in (Cawse-Nicholson, et al., 2013b; Chang, and Du, 2004; Wu, et al., 2006; Bajorski, 2009; Schlamm, et al., 2009; Wei, et al., 2009; Bajorski, 2010; Chang, and Xiong, 2010; Chang, et al., 2010; Eches, et al., 2010; Schlamm, et al., 2010; Bajorski, 2011; Chang, et al., 2011; Chang, 2012; Ming, and Dong, 2012; Cawse-Nicholson, 2013; Chang, et al., 2013). However, it will be discussed that most of the noise-based algorithms lose their validity due to the non-linearity of the (K/S) transformation and deviation of the KM subtractive mixing model for dark mixtures.

2.7.4.1 Harsanyi-Farrand-Chang (HFC)

HFC is a popular algorithm, developed by Chang and Due (Chang, and Du, 2004), estimates ID based on the assumption that the eigenvalues of the centered and non-centered covariance matrices become similar for eigenvalues representing noise with the a zero mean. In other words, the eigenvalues of two sets of eigenvalues, corresponding with centered and non-centered covariance matrices, converge at the point were the signal ends and noise begins. Consequently, if \(\hat{\lambda}_1 \geq \hat{\lambda}_2 \geq \cdots \geq \hat{\lambda}_L\) are the eigenvalues of the correlation matrix, and \(\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_L\) are eigenvalues corresponding to the covariance matrix, the spectral dimension, \(l\), is defined as the band number in which \(\hat{\lambda}_l \geq \lambda_l\) (where \(L\) is the total number of bands). This is due to the fact that the signal source will have a contribution to the sample mean and causes the eigenvalues to be different. For the eigenvectors associated with noise, \(\hat{\lambda}_{1+1} = \cdots = \hat{\lambda}_L = \lambda_{1} = \cdots = \lambda_{l} = \sigma_n\) (\(\sigma_n\) is standard deviation of noise).
Since this difference will never be zero in practice, a statistical analysis is required to find the threshold of the significant differences. The method by Harsanyi, et al. (Harsanyi, and Chang, 1994), proposed a hypothesis test to maximize the likelihood of detection and minimize false alarm probabilities. The hypothesis test can be expressed as follows:

\[ H_0: z_l = \hat{\lambda}_l - \lambda_l = 0 \quad \text{Eq. 2.36} \]

versus

\[ H_1: z_l = \hat{\lambda}_l - \lambda_l > 0 \quad \text{Eq. 2.37} \]

Therefore, the ID will be estimated according to a defined threshold specifying significant differences between two sets of eigenvalues. The HFC method has been improved so that the noise variances are equal in all spectral bands by performing a noise-whitening step, analogous to MNF, prior to the original HFC method (Chang, 2013).

2.7.4.2 Orthogonal Subspace Projection (OSP)

The OSP method (Chang, et al., 2011) estimates ID according to the projection matrix of calculated endmembers. If there are \( p \) signatures, \( \{s_1, s_2, \ldots, s_p\} \) in the spectral image, the \( i \)-th pixel of the spectral image, \( r_i \), can be express as the linear mixtures of those \( p \) signatures as follows:

\[ r_i = S_p \alpha_i + n_i \quad \text{Eq. 2.38} \]

where \( \alpha_i \) denotes the propositions of the endmembers and \( n_i \) is the additive noise. The sample mean vector, \( \mu \), can be expressed by

\[ \mu = \left( \frac{1}{N} \right) [S_p \bar{\alpha}_p] + \bar{n}. \quad \text{Eq. 2.39} \]

In this equation, \( \bar{\alpha}_p = \left( \frac{1}{N} \right) \Sigma_{i=1}^{N} \alpha_i \) and \( \bar{n} = \left( \frac{1}{N} \right) \Sigma_{i=1}^{N} n_i \). Defining projection matrix of the endmember matrix \( S_p \) as \( P_p = S_p \left( S_p^T S_p \right)^{-1} S_p^T \), following formulation can be derived:
\[ E \left[ (P_p \mu)(P_p \mu)^T \right] = S_p \bar{\alpha}_p \bar{\alpha}_p^T S_p^T + P_p^T R_\pi P_p \]  
Eq. 2.40

where \( R_\pi = \left( \frac{1}{N} \right) \sum_{i=1}^{N} n_i n_i^T \). The orthogonal subspace projection of matrix the set of \( p \) endmembers, OSP(\( p \)) is defined as follows:

\[ \text{OSP}(p) = E \left[ (P_p \mu)(P_p \mu)^T \right] = \text{trace} \{ S_p \bar{\alpha}_p \bar{\alpha}_p^T S_p^T + P_p^T R_\pi P_p \} \]  
Eq. 2.41

When the noise covariance is neglected, OSP(\( p \)) can be approximated as:

\[ \text{OSP}(p) = S_p \bar{\alpha}_p \bar{\alpha}_p^T S_p^T. \]  
Eq. 2.42

Theoretically, it can be proven that OSP(\( p \)) is proportion to the number of signature, \( p \). The virtual dimensionality (VD) is estimated for a given threshold \( \varepsilon \), using two gradient and subtractive methods, indicated by \( \nabla \) and \(-\) superscripts respectively, as follows:

\[ \text{VD}^{\text{OSP}, \nabla} (\varepsilon) = \arg \left\{ \min_{1 \leq p \leq L} \left| \frac{\text{OSP}(p + 1)}{\text{OSP}(p)} - \frac{\text{OSP}(p)}{\text{OSP}(p - 1)} \right| < \varepsilon \right\} \]  
Eq. 2.43

and

\[ \text{VD}^{\text{OSP}, -} (\varepsilon) = \arg \left\{ \min_{1 \leq p \leq L} |\text{OSP}(p + 1) - \text{OSP}(p)| < \varepsilon \right\} \]  
Eq. 2.44

The value \( \varepsilon \) is usually selected manually according to a sudden drop or a clear gap between two successive OSP values. It should be noted that other than \( \varepsilon \), an estimation of endmembers, \( S_p \), is also required for calculating VD^{OSP}. Accordingly, different endmember extraction methods result in different VD^{OSP} values.

### 2.7.4.3 Signal Subspace Estimation (SSE)

SSE (Chang, 2013) is similar to OPS, but the interaction of noise has not been neglected. In this method, OPS has been modified by assuming a Gaussian noise with zero mean and noise covariance matrix of \( R_\pi = \left( \frac{1}{N} \right) \sum_{i=1}^{N} n_i n_i^T \). SSE estimates the
number of spectral signatures according to the dimensionality of the data by optimizing \( p \) to minimize the objective function:

\[
VD_{\text{SSE}} = \arg \left\{ \min_{1 \leq p \leq L} \left( \mathbf{r}^T \hat{\mathbf{P}}_p \mathbf{r} + 2 \text{trace} \left[ \frac{\hat{\mathbf{P}}_p \mathbf{R} \mathbf{r}}{N} \right] \right) \right\} \tag{Eq. 2.45}
\]

where \( \hat{\mathbf{P}}_p = \mathbf{S}_p \mathbf{S}_p^T \), \( \mathbf{r} = \left( \frac{1}{N} \right) \sum_{l=1}^{N} \mathbf{r}_l \). HySime is another method for estimating the DI as an improvement to SSE method. In this method, the projection of individual signal vectors (as opposed to the mean values in SSE) is considered for minimization. The simplified form of the equation is shown in Eq. 2.46.

\[
VD_{\text{HySime}}^{\text{DSP}} = \arg \left\{ \min_{1 \leq p \leq L} \left( \sum_{j=1}^{p} \left( -v_j + 2\sigma_j^2 \right) \right) \right\} \tag{Eq. 2.46}
\]

In this equation \( v_j \) and \( \sigma_j^2 \) are eigenvalues of the signal and noise covariance matrix respectively.

### 2.7.4.4 Random Matrix Theory (RMT)

RMT is based on the research by Kritchman and Nadler (Kritchman, and Nadler, 2008) to determine eigenvalues corresponded to noise and signal in the field of chemical unmixing. The advantage of the model is that no parameters need to be adjusted by the user since the false alarm probability is assumed to be fixed for all of the images. Wishart distributions form the core of RMT-based methods. It can be proven that the cross-product matrix, \( \mathbf{A} = \mathbf{X X}^T \), has the Wishart distribution \( W_p(N,\Sigma) \) with \( N \) degree of freedom and joint probability distribution \( \Sigma \). \( \mathbf{X} \) is a matrix with \( N \) independent column vectors each following a \( p \)-variant Gaussian distribution \( N(\mu,\Sigma) \).

For random noise with zero mean and standard deviation of identity, \( N(0, I_p) \), the Wishart distribution has a joint probability distribution of identity matrix, \( W_p(N, I_p) \).

If the noise image has dissimilar variance for each band and therefore normal distribution function of \( N(0, \sigma^2 I_p) \), then the covariance matrix of the noise image will have the Wishart distribution of \( W_p(N, \sigma^2 I_p/N) \). RMT determines the ID by comparing the eigenvalues of the observation covariance matrix to the largest eigenvalues from...
the Wishart distribution. This eigenvalue is determined to be the largest eigenvalues occurring from the noise. Consequently, the ID is determined by deriving a probability distribution function for the largest eigenvalues of Wishart distribution when the number of spectral pixel is much larger than the spectral bands. Each of the eigenvalues is compared against the defined distribution of the largest eigenvalue of noise, according to a hypothesis test and chosen significant coefficients (α=0.5% for all the images). It can be shown that for a large number of pixels, the algorithm is not sensitive to the choice of α. Eventually, all the eigenvectors larger than the defined distribution are assumed to be corresponding to the signal (Cawse-Nicholson, et al., 2013b; Cawse-Nicholson, 2013).

2.7.4.5 Gram Matrix

Messinger, et. al., (Messinger, et al., 2010) introduced a method based on the determinant of the projection matrix, also called Gram Matrix, for determining the ID. The algorithm take advantage of the fact that the volume of the convex hull moves toward zero by adding dependent vectors to an available set of endmembers. It starts by choosing a minimum number of endmembers in a hyper-spectral space. The Gram Matrix, $G$, is defined as the matrix comprised of all cross-production of the chosen endmembers representing the correlations of chosen endmembers, $e$:

$$G_{ij} = <e_i, e_j> \quad \text{Eq. 2.47}$$

The determinant of the Gram Matrix is proportional to the volume of the matrix as a single number of the dependency of the chosen endmembers. Adding a non-independent vector to the endmember selection in a higher dimension leads the determinant to become zero as an indicator for selecting the DI of the spectral data.

2.8 Subtractive Mixing Model

As already explained, the development of any pigment identification pipeline relies on a subtractive mixing model to interrelate mixtures spectral properties in terms of primary pigment concentrations and spectral shape. Kubelka-Munk (KM) is one of the most common theories describing the spectral behavior of isotropic mixtures (Kubelka, and Munk, 1931; Kubelka, 1948). Rather accurate predictions and the
ease of development, formulation, interpretation and evaluations have made this theory more applicable over other available theories. The simplicity of the KM model becomes even more beneficial with the advent of more affordable spectral images when a huge number of pixels is the subject of examination. It has coincided with the demand for spectral analysis of spectral images of the paintings in museums as a novel field of applications for KM-based mixing models (Berns, et al., 2002; Zhao, et al., 2006; Zhao, et al., 2008). Pigment identification, inpainting, and appearance simulations are some examples of spectral analysis of paintings using KM theory (Ciliberto, and Spoto, 2000; Berns, et al., 2002; Berns, and Mohammadi, 2007; Zhao, 2008; Pinna, et al., 2009).

KM theory was derived according to a particular case inherent in a more fundamental and general theory developed by Schuster in astrophysics to describe the scattering, absorption and emission of light in a stellar atmosphere (Schuster, 1905; Kubelka, and Munk, 1931; Kubelka, 1948). Schuster theory, in turn, can be interpreted as a simplified form of the later radiative transfer (RT) theory developed by Chandrasekhar (Chandrasekhar, 1960). RT theory covers a wide range of light and matter circumstances, but is too complicated to be implemented in practice, even for simple cases. In addition, the characterization demands rather large numbers of training samples and sophisticated equipment to specify the model coefficients. These limitations pushed research into a more simplified and practical derivation. Kubleka and Munk (Vargas, and Niklasson, 1997; Neuman, and Edström, 2010a; Neuman, and Edström, 2010b) proposed a two-flux theory based on the former theory introduced by Schuster (Schuster, 1905) and by neglecting the parameters dealing with self-luminous radiations. The formulation procedure provided by Kubleka and Munk along with the Saunderson surface correction performs well for practical uses in paint layers, textile, and paper industries so that more complicated four-flux or many flux theories have been found to be unnecessary (Billmeyer, et al., 1973b; McDonald, 1997; Vargas, and Niklasson, 1997; Berns, and Mohammadi, 2007). Accordingly, KM theory has become the core part of
most of the computer-based color matching software packages in the paint and pigment industries.

The simplicity of KM theory is the result of several assumptions, which is specifically valid for subtractive mixing of conventional pigments and dyes for a wide range of concentrations. Despite reasonable predictions of KM theory of general mixtures of pigments in paint layers, its application for paint mixtures and pigment identification algorithms for paintings needs further evaluations (Berns, et al., 2008). In contrast to the common use of KM theory for spectral estimation of highly scattering mixtures, paintings are usually comprised of dark and weakly scattering components, which is a weak area of KM theory (Billmeyer, et al., 1973a) that necessitates further discrimination for dark mixtures in paintings.

The general form of the KM theory characterizes the optical properties of an isotopic medium according to its absorption (K) and scattering (S) coefficients. Since each primary is defined using two coefficients, this method is also called two-constant KM (2-KM). The incident light also is also assumed to be diffuse and only in two opposite directions. Whereas only two fluxes of diffuse light are taken into account, its application is restricted to isotropic layers with low absorption under a diffuse illumination condition (Vargas, and Niklasson, 1997).

The general form of the KM theory is derived by solving two differential equations for a thin layer of the medium according to its absorption and scattering traits. The integration of the differential equation over the thickness of the layer, \(X\), leads to the following equation:

\[
R = \frac{1 - R_g (a - bcothbSX)}{a - R_g + bcothbSX}
\]

Eq. 2.48

where

\[
a = 1 + \left(\frac{K}{S}\right), \quad b = (a^2 - 1)^{\frac{1}{2}}
\]

Eq. 2.49
In these equations, $R$ is the reflectance factor within the paint layer; $R_g$ is the spectral reflectance of the background or substrate; $K$ and $S$ are KM effective absorption and scattering coefficients (which are different from the actual physical absorption and scattering of the particles). If the medium layer is optically opaque (or when $X \to \infty$) the equation is simplified as follows:

$$R_\infty = 1 + \left(\frac{K}{S}\right) - \left[\left(\frac{K}{S}\right)^2 + 2\left(\frac{K}{S}\right)^1\right]$$ \hspace{1cm} \text{Eq. 2.50}

or

$$\left(\frac{K}{S}\right) = \frac{(1 - R_\infty)^2}{2R_\infty}$$ \hspace{1cm} \text{Eq. 2.51}

Considering Eq. 2.50 and Eq. 2.51, the spectral properties of any paint layers of infinite thickness can be calculated by knowing $K$ and $S$ coefficients of the isotropic layer. $K$ and $S$ coefficients of any mixture are estimated by a linear combination of $K$ and $S$ coefficients of the primary pigments, weighted by the concentration of each component introduced by Duncan (Duncan, 1940):

$$K_{mix} = \sum_{i=1}^{n} c_i k_i$$ \hspace{1cm} \text{Eq. 2.52}

$$S_{mix} = \sum_{i=1}^{n} c_i s_i$$ \hspace{1cm} \text{Eq. 2.53}

where $k$ and $s$ denote the unit scattering and absorption per concentration. Subscripts $mix$ and $i$ refer to “mixture” and “$i$-th” component respectively; $c$ is the portion or concentration of each component and $n$ is the total number of primary pigments in the mixture. For an opaque layer, the following equation can be derived from Eq. 2.51, Eq. 2.52 and Eq. 2.53:

$$\frac{(1 - R_{\infty,mix})^2}{2R_{\infty,mix}} = \left(\frac{K}{S}\right)_{mix} = \frac{\sum_{i=1}^{n} c_i k_i}{\sum_{i=1}^{n} c_i s_i}$$ \hspace{1cm} \text{Eq. 2.54}
In practice, Eq. 2.54 is a simple but non-linear formula characterizing the behavior of a mixture based on the total scattering \((c_i s_i)\) and absorption \((c_i k_i)\) of each component. Both \(k\) and \(s\) values are required to be estimated for each pigment. The \(k\) and \(s\) coefficients of each pigment are usually derived practically by rewriting the equations with respect to \(k\) and \(s\) coefficients and solving them for a set of training data with known spectral reflectance. Several methods have been proposed to calculate the \(k\) and \(s\) coefficients for 2-KM theory (Allen, 1980; Walowit, et al., 1987; Berns, 2000; Zhao, and Berns, 2009). Using a series of pigment mixture with a white component (known as a tint ladder) is a common way of calculating \(k\) and \(s\) for each pigment. Although a tint ladder of only two known mixtures is enough for solving the equation for \(k\) and \(s\) coefficients mathematically, a larger number of training mixtures is used in practice. KM coefficients are derived using regression methods if the total number of training mixtures are larger than two (Walowit, et al., 1988). Berns and Mohammadi (2007) discussed the influence of training dataset on the estimated KM coefficients for pigment selection in inpainting and conservation processes and concluded that a training set comprised of only two components of masstone and tint (a mixture of the colorant and white that has near-maximum chroma for a given pigment) produces sufficient performance in estimating the \(k\) and \(s\) coefficients in the 2-MK theory. This approach reduces the complexity of the formulations noticeably with no regression calculations required; however, the evaluation did not include a uniform distribution of pigment concentrations of light and dark mixtures. In addition, the evaluating datasets were limited to the mixtures of each pigment and a white component. On the other hand, the estimated coefficients might not be optimized for regular mixtures of more than one pigments due to inaccurate estimations of KM theory for highly absorbing mixtures.

### 2.8.1 Single-Constant Kubelka-Munk

Single-Constant Kubelka-Munk (KM) theory is a subtractive mixing model capable of predicting the optical property of a mixture based on a linear combination of its primary components. Regardless of applicability limitations, the linear nature of the equations distinguishes this theory from other complicated and non-linear mixing
models, which makes the single-constant KM theory the first candidate for most pigment-based image-processing tasks, such as inpainting and pigment identification. However, this simplicity is the result of several physical and mathematical assumptions limiting the accuracy, precision and applicability of the theory.

Single-constant KM (1-KM) theory is a derivation of more comprehensive theories; hence, its performance is also narrowed by the former simplifications. The original KM theory therefore acts effectively for limited forms of matter (isotropic) and lighting geometries (diffuse), which are specifically valid for subtractive mixing of conventional pigments and dyes (Billmeyer, et al., 1973b; McDonald, 1997; Vargas, and Niklasson, 1997; Berns, and Mohammadi, 2007; Neuman, and Edström, 2010a; Neuman, and Edström, 2010b). A drawback of the theory is the long processing time when a massive numbers of pixels are involved. 1-KM theory can be considered a remedy of this problem. This theory is the result of an extra modification of the two-constant KM (2-KM) theory, wherein the scattering of the medium layer is assumed to be supplied by the white component introduced by Davidson and Hemmendinger (Davidson, et al., 1963; Davidson, and Hemmendinger 1966). In contrast to the 2-KM theory, 1-KM has some distinctive characteristics by delivering linearity and convexity to the ratio of $K$ and $S$ coefficients, also known as ($K/S$) space, as a linear subtractive mixing model. These characteristics enable the use of a variety of algorithms available in linear algebra and signal processing with reasonable speed for analyzing the spectral data beneficial in pigment mapping and pigment identification for paintings (Berns, 1997; Berns, et al., 2002; Berns, and Mohammadi, 2007).

1-KM has been found to be applicable in textile, paper and paint, whereby the concentration of color pigment is small compared to the white substrate (Allen, 1980; McDonald, 1997; Berns, 2000; Berns, and Mohammadi, 2007). Unfortunately, the 1-KM theory does not provide a perfect linearity for the paint layers since the presumed assumptions are not met (Billmeyer, et al., 1973b; Berns, and
Mohammadi, 2007). This deviation causes some errors in pigment predictions and analysis, as mentioned in previous research (Berns, and Imai, 2002; Berns, et al., 2002; Zhao, et al., 2008). As a conclusion, none of the current KM mixing theories is exclusively appropriate for spectral processes associated with spectral images of paintings.

1-KM theory is derived from 2-KM theory where the scattering of the medium is overcome by the white component or the substrate. This assumption can be applied to Eq. 7 by neglecting the scattering of chromatic components and setting them to zero:

\[
\left( \frac{K}{S} \right)_{mix} = \frac{c_w k_w + \sum_{i=1}^{n} c_i k_i}{c_w s_w}
\]

Eq. 2.55

\[
\left( \frac{K}{S} \right)_{mix} = \left( \frac{k}{s} \right)_w + \sum_{i=1}^{n} \left( \frac{c_i}{c_w} \right) \left( \frac{k_i}{s_w} \right)
\]

Eq. 2.56

In these equations, subscript \( w \) refers to the white pigment (in the paint layers) or substrate (in paper or textiles); \( n \) is the total number of primary chromatic pigments. The reflectance of the mixture can be estimated based on the linear combination of the \( K/S_w \) ratio of each component. The linearity of the formula is a considerable advantage for analyzing of the large number of pixels, as well as optimization methods. In addition, since only a single coefficient is necessary to be specified for each primary, fewer numbers of training samples are usually required for mixture characterizations.

The drawback of the 1-KM model is its poor predictions for the high-scattering pigments and pure mixtures; high-scattering pigments violate the required condition for 1-KM to be valid. Also, in cases where the concentration of the white component decreases, the denominator moves towards zero and makes the equations unreliable. Based on this formulation, masststones have an unrealistic
spectral reflectance of zero for opaque layers because of zero scattering assumptions.

2.8.2 Saunderson Correction

Saunderson correction is strongly recommended by several researchers (Kuehni, 1975; Allen, 1980; Völz, 1995; McDonald, 1997; Berns, 2000; Berns, and Mohammadi, 2007; Klein, 2010) prior to KM calculations. It takes into account the internal and external specular reflectance due to changes in the refractive indices on the surface of the film layer. The original equation was provided by Ryde (Ryde, 1931; Ryde, and Cooper, 1931) and later Saunderson applied the Ryde correction equation to the color formulation of opaque-pigmented plastics using the KM theory (Saunderson, 1942). The Saunderson equations for di:8° geometry are shown in Eq. 2.57 and Eq. 2.58 (McDonald, 1987).

\[
R_m = \frac{(1 - k_1)(1 - k_2)R_i}{1 - k_2R_i} + k_1 \tag{Eq. 2.57}
\]

\[
R_i = \frac{R_m}{(1 - k_1)(1 - k_2) + k_2R_m - k_1k_2} \tag{Eq. 2.58}
\]

The equation corrects the measured reflectance, \( R_m \), for surface reflections. The corrected reflectance is called internal reflectance, \( R_i \), which describes the true amount of diffuse light inside the paint layer. \( k_1 \) and \( k_2 \) are the proportion of reflected light on external and internal surfaces. Even though the coefficients are specified for particular measurement geometries, materials and incident light angles (Ryde, and Cooper, 1931; McDonald, 1987), it is recommended to apply an additional optimization algorithm to achieve the best quantities (Berns, 2000).

2.9 Simulation and Visualization

Software development and visualization the algorithms on actual images artworks are another important aspect of spectral imaging pipelines (Taplin, and Berns, 2005). Virtual representations of the artwork provide simulations of the variety of the treatments particularly when the practical manipulation of the artwork is not
desirable. Varnish cleaning, restoration and inpainting processes are some of the examples can be simulated, visualized and evaluated before any actual treatments on the painting. In addition some cases are limited only to digital simulation of the painting such as color reconstruction of a faded pigment in a particular painting (Martinez, et al., 2002; Cappellini, and Piva, 2006; Fischer, and Kakoulli, 2006; MacDonald, 2006).

In fact, common spectral capturing systems are computationally expensive, specifically for high-resolution imaging purposes (Zhao, et al., 2006; Zhao, 2008; Zhao, et al., 2008). In most cases, the spectral analyses can be applied to only a small portion of the painting. In addition, spectral workflows rely on time-consuming and costly spectral images. Considering the final users of the captured images, which are mostly artists and photographers, implemented workflow should be user-friendly and optimized so that it can be applied to high-resolution images in a reasonable interval of time.
A well-characterized spectral acquisition system is a vital piece of a spectral-based pigment identification (PI) pipeline. The spectral quality of the acquired data must fulfill a certain level of accuracy, sufficient for distinguishing pigment signatures within a painting. Of the common spectral imaging systems discussed in Section 2.3, a liquid crystal tunable filter (LCTF)-based capturing system was chosen for spectral measurements considering spectral accuracy, repeatability, cost and measurement time. This chapter details the implementation and evaluation of a target-based spectral characterization workflow for an LCTF-based imaging system.

The target-based color characterization of capturing systems has been the subject of many research papers in the past decade (Hong, et al., 2001; Barnard, and Funt, 2002; Li, et al., 2003; Martínez Verdú, et al., 2003; Cheung, and Westland, 2004; Cheung, et al., 2004a; Cheung, et al., 2004b; Nyström, 2007; Fairchild, et al., 2008; G. D. Finlayson, 2011). The conclusions mostly point out that the target-based characterization methods are valid for a particular lighting geometry, color target
materials and surface structure. This dependency has led to designing optimized color targets in recent research taking into account several factors, such as material, surface properties, gamut, and the number of color patches, with less consideration of the role of lighting geometry on the target’s appearance. The variety of capturing geometries and the uncontrolled nature thereof increase the complexity of the characterization process (Hong, et al., 2001; Green, and MacDonald, 2002; Sharma, 2003). The material aspects become important particularly when color patches vary in surface and spectral properties, leading to different appearance changes according to geometry changes. The material and geometry dissimilarities are common cases for colorimetric and spectral acquisition of paintings in museums; therefore the dependency of target-based camera characterization with respect to the target’s surface structure and acquisition geometry was investigated. It will be discussed that this dependency on capturing conditions can be predicted and in turn reduced by compensating for geometry and surface characteristics using an appropriate optical model.

The results were extended for an LCTF-based multispectral imaging system. It also will be discussed that additional corrections are required to compensate for angular dependency of LCTF transmissions and geometry dissimilarities. Eventually, the corrected camera signals were converted to spectral reflectance using the Berns-Petersen spectral reconstruction algorithm based on preliminary research explained in Ref. (Hensley, and Wyble, 2012).

3.1 Camera Calibration and Geometry Corrections

Most of the camera characterization models are based on the linear model as explained in Section 2.4. In spite of the linear relationship of CCD- and CMOS- based sensor responses and incident light irradiance, implementing an accurate transformation is not straightforward when target-based methods are used. Geometry dissimilarity is already a known source of estimation errors, particularly
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in target-based spectral characterization workflows; however no practical solutions have been introduced (Hubel, et al., 1997; Sharma, 2003).

In this section a comprehensive workflow for camera calibration and characterization is investigated. The calibration process addresses the influence of geometry differences as a source of non-linearity. This non-linearity is corrected using a physical model describing the spectrophotometric changes according to illumination/capturing geometries.

Simple polynomial-based regression methods have been introduced as practical and simple models with satisfactory accuracy compared to other methods. In most of the proposed methods, camera responses are required to be RAW data and already corrected for non-linearity, dark current and optical flare. In many cases, a simple linear transformation is sufficient to map device-dependent and device-independent spaces with adequate performance; even so, higher-order polynomials have reportedly improved estimations (Hong, et al., 2001). It is also mentioned that the lower order conversions are preferred to avoid unwanted local maxima and minima in the transformation, as well as over fitting systematic errors, which cause dependency on specific capturing conditions (Green, and MacDonald, 2002; Sharma, 2003). It will be discussed that a part of current characterization limitations is due to the differences of the lighting and viewing geometries influencing material appearance. For example, matte and glossy surfaces appear differently in 45:0 geometry despite similar reflectance factor where measured by a d:0 spectrophotometer. Two objects may have similar reflectance factor for a particular viewing geometry, but differ for other lighting conditions. As a result further information, i.e., either surface characteristics or the geometrical conditions, should be provided in addition to the spectral data for a more comprehensive description of the surface characteristics. This consideration needs a model for describing the surface properties in a variety of illumination/capturing conditions such as the bidirectional reflectance distribution function (BRDF) (Dorsey, et al., 2008). However, in addition to the complexity in obtaining BRDF data, they cannot be used
unless the capturing geometry is known precisely. In most cases, none of the mentioned requirements are easily accessible. On the other hand, training targets for camera characterization typically have isotropic uniform surfaces, which can be described by simpler surface correction methods, such as the Ward model (Ward, 1992) or the Saunderson equation (Saunderson, 1942; Völz, 1995). The Saunderson correction is commonly used in colorant formulation, accounting for spectrophotometer geometry, which was selected for use in this research.

The Saunderson correction relates the internal and external reflections due to changes in the refractive index at the surface of a paint layer as explained in Section 2.8.2. The equation corrects the measured reflectance, \( R_m \), for surface reflections. The corrected reflectance is called internal reflectance, \( R_i \), which is independent of the surface structure. The general form of the Saunderson equation is shown in Eq. 3.1 and Eq. 3.2

\[
R_m = \frac{(1 - k_1)(1 - k_2)R_i}{1 - k_2R_i} + k_{ins}k_1 \tag{Eq. 3.1}
\]

\[
R_i = \frac{R_m - k_{ins}k_1}{(1 - k_1)(1 - k_2) + k_2R_m - k_{ins}k_1k_2} \tag{Eq. 3.2}
\]

These equations are slightly different from those mentioned in Section 2.8.2 by adding the new term \( k_{ins} \). The \( k_{ins} \) was used by Saunderson in his original paper (Saunderson, 1942). More explanation of the term was provided by the latter authors (McDonald, 1987; Völz, 1995). The variables \( k_1 \) and \( k_2 \) are wavelength dependent coefficients specifying reflection portion at the surface for light incident from outside and inside, respectively. However, these values are generally assumed to be constant in all the visible wavelengths including this research. The Saunderson coefficients have already been calculated and optimized for specific measurement geometries, materials and incident light angles, according to available spectrophotometer geometries (Ryde, 1931; Ryde, and Cooper, 1931; Saunderson, 1942; McDonald, 1997). \( k_1 \) is specified using the Fresnel equation as a function of incident angle and refractive index of the surface suggested to set to 0.040 for parallel light and 0° incident angle and 0.092 for diffuse lighting geometries (for a
media with refractive index of about 1.5. $k_2$ is usually determined experimentally because most materials are not perfect isotropic scatterers and it is difficult to have an accurate description of the internal specular reflectance within the pigmented layers (Ryde, 1931). The recommended values for paint layers vary between 0.4 and 0.6 according to the refractive index, surface properties and the lighting geometry (Saunderson, 1942; Völz, 1995). $k_{ins}$ describes the geometry of the measurement determining the proportion of the external reflected light received by the detector. It is important to note that the Saunderson coefficients ($k_1$, $k_2$ and $k_{ins}$) change according to the lighting and measurement geometries. Accurate calculation of the coefficients is not always practical even for a particular spectrophotometer with known geometry. Hence, it is recommended to apply an additional optimization algorithm to optimize these quantities (Berns, 2000). The Saunderson equation can be applied with the same manner but for image capturing systems as measurement devices. The correction imposes the difference between the spectral radiance reaching the camera and the spectrophotometer used to measure the calibration target. Looking at Eq. 3.1 and Eq. 3.2, the Saunderson equation is a function of three coefficients, which makes the model simple and easy to implement.

The main difference between a conventional and the surface-corrected method is illustrated in Figure 3.1. In conventional characterization methods (Figure 3.1 (a)), camera signals are converted to the tristimulus values of a specific spectrophotometer. Notice that the characterization algorithm connects two different geometries. Hence, multispectral camera responses do not match with those of a spectrophotometer. A more appropriate alternative is to interrelate camera signals and spectral radiance of the seen, using a spectroradiometer in the similar geometry. This approach, however, requires rather expensive and time-consuming radiometry measurements. Additionally, spectrophotometric data of color target are usually available for specific geometry, which eliminates the necessity of spectral measurement for camera characterization purposes in the condition of geometry compensation.
In the proposed method (Figure 3.1(b)), the reflectance factor data of the color targets are corrected, corresponding to the camera-taking geometry. Thus, the characterization algorithm transforms spectral reflectances in the same geometry. In practice the reflectance data of two geometries are corrected using the internal reflectance, $R_n$, as a geometry-independent connection space.

Figure 3.1: The characterization workflow for typical (a) and proposed (b) methods.

Figure 3.2 is a flowchart of the process for the proposed reflectance correction. The reflectance factor from the spectrophotometer, $R_m$, is converted to internal reflectance using Eq. 3.1 and according to the geometry of the spectrophotometer.
Afterward, the internal reflectance is converted to reflectance factor of the geometry of the camera-taking system, $R_{m,c}$. In fact, the whole process is a model for characterizing the surface property that converts the reflectance factor among different illumination and capturing geometries. By a simple replacement of $R_m$ with new coefficients in Eq. 3.2, reflectance values for the second geometry ($R_{m,c}$) can be calculated as a single equation:

$$R_{m,c} = \frac{(1 - k_1)(1 - k_2)(R_m - k_{ins}k')}{(1 - k_1')(1 - k_2') - k_{ins}'k_1'k_2' + k_{ins}'k_1'k_2 + R_m(k_2 - k_2')} + k_{ins}k_1 \quad \text{Eq. 3.3}$$

In this equation, $k_1'$, $k_2'$, $k_{ins}'$ are the Saunderson coefficients corresponding to the second (or camera-taking) capturing geometry.

![Diagram](image1.png)

**Figure 3.2:** The workflow of correcting the measured reflectance for different geometries.

Since the capturing geometry is not accurately known for the image-capturing system, the Saunderson coefficients are determined using an iteration loop to achieve the best possible linearity between camera responses and tristimulus values after surface correction. Figure 3.3 is a diagram of the coefficient optimization by minimizing spectral reflectance RMS error.

![Diagram](image2.png)

**Figure 3.3:** The workflow of optimising model coefficients by minimizing spectral RMS values.
According to regular characterization workflows, camera signals must already be corrected for dark current, optical flare and linearization so that the actual entrance radiance is represented as a linear combination of the output signals (or camera responses) (Barnard, and Funt, 2002; Green, and MacDonald, 2002; Sharma, 2003; Westland, et al., 2004). Flat-field and dark-current/optical-flare corrections were applied to the captured images in advance of any further processing. Dark current is defined as the sensor readings when no incident light exists. Dark current of the camera is measured by acquiring camera signals with the camera cap on. Flare causes an unwanted increase of camera response due to stray light to the camera lens and varies according with the scene content (e.g. flare is larger for scene with a light background). The dark current and flare corrected camera signals are obtained by subtracting the dark current/flare values from the camera. A light trap made for dark calibration of the Color-Eye 7000 spectrophotometer, shown in Figure 3.4, was utilized for flare corrections. Since the optical flare is variable from scene to scene, the optical flare and dark-current correction were performed for each image independently. Afterwards, the collected images were rectified for lighting non-uniformities and lens fall-off using a flat uniform surface of Fluorilon (with the surface close to that of a Lambertian surface), known as flat-field correction. Further explanation of each term can be found in Ref. (Reinhard, et al., 2008).

Figure 3.4: Light trap for measuring dark current and flare [Color-Eye® 7000A manual, www.xrite.com].
It must be remembered that the optimized coefficients \((k_1, k_2, k_{ins}, k_1', k_2', k_{ins}')\) are relative values with no physical meaning because different Saunderson coefficients can produce identical results. The reason is that only three coefficients (rather than six) are sufficient to optimize Eq. 3.3. Mathematically, Eq. 3.3 can be written in a simpler form as a function of three variables:

\[
R_m' = \frac{R_m + \alpha}{\beta R_m + \gamma}
\]

Eq. 3.4

where, coefficients \(\alpha, \beta \text{ and } \gamma\) are functions of the Saunderson coefficients for both measuring and capturing geometries. The calculation of Eq. 3.4 is shown in Appendix A. As a result, using the equation with six variables \((k_1, k_2, k_{ins}, k_1', k_2', k_{ins}')\) leads to an ill-posed system of equations. One alternative to converge the coefficients to feasible values is to fix the first Saunderson coefficients (three variables \(k_1, k_2\) and \(k_{ins}\)) to predefined values for the utilized spectrophotometer with a known geometry.

More simplifications can be made with respect to physical facts. As an example, Eq. 3.3 can be expressed in a simpler form by considering the physical facts about the internal reflectance within the paint surface. The internal reflectance, \(k_2\) and \(k_2'\) should be identical for isotropic pigmented layers because the incident light will be diffused similarly inside the paint layers independent of light incident angle. This assumption leads to a simpler form of the equation, with only two free variables:

\[
R_{m,c} = \mu R_m + \rho.
\]

Eq. 3.5

where coefficients \(\mu\) and \(\rho\) are also functions of Saunderson coefficients. More details are provided in Appendix B.

### 3.1.1 Experimental

Reflectance factor data of a set of gray patches were measured by two spectrophotometers and a tele-spectroradiometer. A Photo Research PR-655 SpectroScan tele-spectroradiometer (PR-655) was used for the radiance
measurements. The Xrite i1 with 45°:0° geometry and Color-Eye 7000 with di:8° and de:8° geometries were used for spectrophotometric measurements. The set of gray patches was made by mixing different concentrations of matte (carbon black and titanium white of Golden Matte liquid acrylic paints) and glossy (black and white paints of Sherwin Williams Acrylic high-gloss latex paints) paints. The gray scale contains 14 patches with the glossy and the matte gray surfaces, shown in Figure 3.5. The gray patches were approximately spectrally non-selective so as to be insensitive to the errors of wavelength misalignments and bandwidth differences between the spectrophotometers and the spectroradiometer. When the PR-655 was used, the reflectance factor of each sample was extracted using pressed PTFE as a reference white. PTFE has a reflectance factor of almost one in all visible wavelengths and a matte surface close to a Lambertian surface. The measurements were conducted for three different lighting and capturing geometries as shown in Figure 3.6. The spectral properties of the patches were the average of at least three measurements to reduce the noise, particularly for dark samples.

Figure 3.5: Gray scale with 14 glossy, matte and semi-glossy patches.

In order to achieve a constant lighting and capturing geometry, the position of the PR-655 was kept fixed and each sample was repositioned. In the first geometry, the target was imaged under a GTI EVS light booth with a diffuse fluorescent simulated D50 lighting (Figure 3.6 (a)).
In the second geometry, two directional lights (Buhlite Soft Cube light Sc-150) at almost 45° from the normal were used for illumination (45°/0°-dual light geometry). The spectroradiometer was placed approximately at the normal axis of the target surface (Figure 3.6 (b)). This geometry fit the best with the proposed geometry recommended by ISO17321 (Section 4.3.3) for target-based illumination geometry [14]. The third geometry is similar to the previous one, but using only one light at 45° of the surface normal, as shown in Figure 3.6 (c) (45°/0°-single light geometry). Four methods were used for geometrical compensations: a) the Saunderson correction corresponding to Eq. 3.3 or Eq. 3.4; b) scaler-offset, referring to a simplified Saunderson as defined by Eq. 3.5; c) scaler; and d) offset, which considers a single scaler and single offset, respectively. The results were compared to a case in which no correction was applied to the reflectance factor data as a metric of geometrical effects on the measured spectra. In all of the experimental phases, a non-linear iterative optimization algorithm based on quadratic programming (fmincon function in Matlab) was used. Initial values were picked according to those recommended in the literature for paint layers. The Saunderson coefficients were constrained to be between zero and unity so that they had physical meaning. Optimization iteration rapidly converged to the optimum values for all of the geometries and different initial values. If all six Saunderson coefficients were optimized, the coefficients would depend on the initial values, even though it did not affect the final error.
3.1.2 Results and discussion

The RMS values between the reflectance factor data measured by the two spectrophotometers and the spectroradiometer for the first phase are compared in Figure 3.7. As explained above, this phase includes spectral matches of glossy and matte samples in three spectrophotometric and three spectroradiometric geometries. When no correction was applied to the reflectance factor data (plotted as not corrected bars in Figure 3.7), the differences are extensive, highlighting that the geometrical changes do influence the measured reflectance factor as expected. The more the geometrical dissimilarities, the larger the spectral differences. For instance, reflectance factor data measured by the Color Eye 7000 di:8° have the largest RMS values compared to reflectances measured by the PR-655 with the 45°/0°-single light geometry. On the other hand, the i1 spectrophotometer produced a good correlation with the 45°/0°-dual lights (which is a symmetrical directional lighting geometry) since they have analogous lighting and capturing characteristics. As expected, selecting spectrophotometers in accordance with the capturing geometries reduces spectral errors. Integrating sphere with specular excluded (de:8°) geometry resulted in smaller RMS values compared to di:8° geometry. It implies that the specular reflectances are smaller for camera-capturing geometries, even compared to di:8° geometry. It explains why di:8° yielded larger errors for all the geometries when no correction was applied. When comparing matte and glossy patches, glossy patches were more sensitive to the geometrical changes. This sensitivity can be either amplified or weakened according to the capturing geometries. For example, diffuse or 45°/0°-dual light geometry with matte patches gave small and similar RMS values regardless of the spectrophotometer geometry. On the contrary, glossy patches in the 45°/0°-single light condition led to distinct results for different spectrophotometric geometries.

The surface correction resulted in almost the same RMS values for all of the capturing geometries (plotted as Saunderson bars in Figure 3.7). For diffuse capturing geometry, the RMS values were slightly larger, which could be caused by
lower illumination level in the diffuse capturing geometry. The results indicate that the Saunderson correction is capable of eliminating the effect of geometric differences. Scalar and offset bars in Figure 3.7 correspond to Eq. 3.5. This method yielded similar RMS values as the Saunderson correction method confirming the validity of the assumption made. It also implies that a characterization method with a 3×4 transformation matrix (by adding the offset coefficients in the regression model) is capable of improving the estimations compared to a 3×3 matrix, but only for certain materials, which is evaluated in the next phase of the experiment.

Neither single scalar nor single offset performed satisfactorily in compensating for the geometrical changes. The single offset correction (indicated by offset bars in Figure 3.7) is particularly effective for the Color-Eye 7000 spectrophotometer with SPIN; nevertheless the RMS errors are still large for some geometries. Likewise, the single scalar correction (indicated by scalar bars in Figure 3.7) could not noticeably address geometrical changes.
It is also important to mention that a single set of the Saunderson coefficients is valid only for either matte or glossy samples; so combinations of matte and glossy samples should not be used for deriving the coefficients or optimizing the transformation matrix. Accordingly, $k$ values optimized for glossy patches cannot be used for matte samples and vice versa. This dissimilarity resulted in greater RMS errors when both matte and glossy patches were utilized for optimization (look at Fig. 7 when 14 matte and glossy samples are utilized).

In summary, the measured reflectance factor data are different according to the surface properties of the samples and the geometry of the measurements. Also the reflectance factor geometrical mismatches can be corrected for a given capturing geometry using the Saunderson equation and minimizing the spectral RMS values. The conclusions drawn in this phase were used for characterizing a trichromatic camera in the second phase of the experiment.

### 3.2 Spectral Reconstruction

A linear optical model for characterizing the capturing system was mentioned previously in Section 2.4. The mathematics of the optical model can be rewritten in simpler terms as in Eq. 3.6. This equation relates the camera response of the $i$-th channel of the camera response ($a_i$) at 2-D position $x$ incident radiant light
(Haneishi, et al., 2000; Hardeberg, 2001a; Ribes, et al., 2008; Ribes, and Schmitt, 2008):

\[ a_i(x) = \int_{\lambda_1}^{\lambda_2} E(\lambda, x)\rho(\lambda, x)S_i(\lambda, x)d\lambda + e_i(x) \]  
Eq. 3.6

The camera responses are defined as the integration of all the radiant energy that reaches the sensor weighted by the sensitivity of the \( i \)-th channel \((S_i)\). The channel sensitivity, \( S \), is the result of filter transmission and the sensitivity of the detector. \( \rho \) and \( E \) are reflectance factor of the surface and the SPD of the light source, respectively. \( \lambda_1 \) and \( \lambda_2 \) determine the measurement wavelength range associate with the sensitivity of the sensor and filter transmissions. \( e_i(x) \) is the measurement noise associated with \( i \)-th channel at location \( x \).

The goal is to estimate \( \rho \) in Eq. 3.6. Since LCTF produces a series of wide band transmissions, the output of each channel is not independent. On the other hand, the camera signals mostly correlate with the neighbor bands. Consequently, a proper estimation of spectral radiance of each band can be obtained as a linear combination of neighborhood bands. Berns and Petersen (Berns, and Petersen, 1988) introduced a similar technique for spectral correction when a sufficient sampling of spectral radiance is available. Camera responses can be thought as spectral radiance of a spectrophotometer and be corrected for varying bandwidth and possible wavelength shift. Using this method, the number of required coefficients was reduced compared to other statistical methods such as pseudo-inverse. The performances of the Berns-Petersen and matrix pseudo inverse-based methods were investigated in another research using a similar acquisition system (Hensley, and Wyble, 2012). The correction equation for converting two classes of reflectance factors \((\rho_i \text{ from spectrophotometer and } a_j \text{ from the acquisition system for } j\text{-th wavelength})\) is as follows:

\[ \rho_j = \beta_{0,j} + \beta_{1,j}a_j + \beta_{2,j}\frac{da_j}{d\lambda} + \beta_{3,j}\frac{da_j^2}{d^2\lambda} \]  
Eq. 3.7
Since the camera signal has been linearized in advance, the nonlinear terms were omitted from the original form of the Berns-Petersen equation (Hensley, and Wyble, 2012). In addition, unlike the original equation provided by Berns-Petersen, the $\beta$ values were optimized as a function of wavelength because wavelength shift and channel bandwidths vary for each wavelength.

It should be remembered that the camera responses must be corrected in terms of linearity, dark current, lens fall-off, flare and spatial illumination uniformity to fit into Eq. 3.6. The linearity of the camera response with the incoming radiance can be evaluated by a set of non-selective gray samples (Moghareh Abed, et al., 2013). The corrected response after flat-fielding, dark current and flare correction, $a_{cr}(x)$, is shown in Eq. 3.8.

$$a_{cr}(x) = \frac{a_{raw}(x) - a_{dc}(x) - (a_{ff} - a_{ff,dc})}{a_{ff}(x) - a_{dc}(x) - (a_{ff,ff} - a_{ff,dc})}$$  

Eq. 3.8

In this equation $a_{raw}$ denotes the raw response of the camera. Subscripts $ff$, $fl$ and $dc$ are camera responses for flat-field, flare and dark current images respectively. $a_{cr}$ is the camera signal corrected for dark current, flare illumination and lens fall-off non-uniformities.

Another spatial non-uniformity associated with the LCTF-based spectral systems is variability of the filter transmissions according to the incident light angle (Baronti, et al., 1998; Liang, et al., 2005; Ribés, et al., 2005). An example of this wavelength shift for a rendered image of a uniform solid red patch is demonstrated in Figure 3.8. It can be seen that the color difference from different parts of the image is perceivable.
Figure 3.8: a) The rendered image of a red solid sample after spectral reconstruction with no angular correction captured using LCTF multispectral imaging system. b) Different sample of the image in five locations of the image specified in the original image (a).

The angular non-uniformity was corrected using six solid uniform color sheets and the Berns-Petersen spectral correction method. Mathematically, the incident angle is a function of segment location; therefore, the correction can be applied based on the pixels’ location. In practice, the correction is applied to larger segments \( s \) since angular changes are negligible within each segment. Accordingly, the same responses are obtained for all the segments for uniform solid color patches. The corrections for each segment were performed using following equation:

\[
a_{s,i} = \gamma_{0,s,i} + \gamma_{1,s,i}a_{cr,c,i} + \gamma_{2,s,i}\frac{da_{cr,c,i}}{d\lambda} + \gamma_{3,s,i}\frac{d^2a_{cr,c,i}}{d\lambda^2}
\]

where \( a_{cr,c} \) is the camera response for segment \( s \) at the center of the image after flat-fielding and dark/flare corrections. \( a_{s,i} \) is corrected response for angular dependency of the measurements. \( \gamma \) coefficients are optimized for each segment so that the camera signal is equal to the signal at the center of the image for all uniform solid patches. \( \gamma \) values are functions of acquisition channel because the angular dependency is different per channel. Eventually, the camera responses are interpolated to match the wavelength range of the training spectral data in a separate step to be used in Eq. 3.7 \((a_i \to a_j)\).
A summary of spectral characterization workflow is schemed in Figure 3.9. All images are corrected for flare and dark current as preliminary steps before next processes. Both flare and dark current subtractions were performed in the same exposure time of each channel. For flat fielding, the dark current/flare corrected camera signals were divided to those of flat-field images as shown in Eq. 3.8. It should be noted that that the angular correction experiment is performed once for a particular capturing geometry. After the coefficients are calculated, they can be used for later measurements. In order to keep the coefficient independency from measurement factors, another flat-field step is placed before the angular correction step. The next flat-fielding process is also required since wavelength correction might affect the previous flat-fielding corrections.

Figure 3.9: The general workflow of spectral characterization.
3.2.1 Experimental

The research was conducted using an LCTF-based spectral imaging. Two HMI light sources (Buhlite Soft Cube light Sc-150) at almost 45° from the normal were used for illumination. The LCTF capturing unit was placed at the normal axis of the target surface (Figure 3.10). This geometry fit the best with the proposed geometry recommended by ISO17321 (Section 4.3.3) for target-based illumination geometry (ISO, 2006). A 1.4 megapixel Lumenera LW165m 16-bit monochrome camera with a Sony ICX285 2/3’ format 9.0x6.7 mm array sensor was used for image acquisition. A CRI Varispec LCTF was utilized for spectral filtration in 29 spectral bands from 435 to 700 nm. Each image was the average of thirty measurements per each channel. The exposure time for each band was adjusted to achieve 80% signal strength for the white sample after removing defected pixels from the captured image. Further technical details are available in Ref. (Hensley and Wyble, 2012).

![Figure 3.10: The LCTF-based capturing system.](image)

Six sheets of Color-aid uniform solid matte samples were used to evaluate and correct the wavelength angular misalignments. Spectral reflectances of the solid samples illustrate that they have enough variation in different regions of the visible spectrum (Figure 3.11). Using six solid samples, γ values in Eq. 3.9 were obtained by
making an over-determined system of equations for each segment. The spectral reflectances of six matte samples are also depicted in Figure 3.11.

![Uniform solid sheets used for angular correction: a) six uniform chromatic sheets b) the spectral reflectance of the uniform samples.](image)

The linearity of the each one of the channels was examined using camera responses of five gray patches of the ColorChecker Passport. The r-square of 1.000 for all 29 channels verified linearity of the camera signals to incident radiant light. Therefore, no further linearity correction was applied to the camera responses.

The linear camera signals were used to optimized $\beta$ values in Eq. 3.7 using 24 samples of a X-rite ColorChecker Passport with matte samples (Figure 3.12). The ColorChecker Passport is a popular and accessible color target, which is being used regularly by photographers for colorimetric calibration. The MCSL paint color target was used for evaluating the characterization process (Figure 3.13). The color target contains different chromatic and achromatic patches, which cover the entire color space adequately. There are two series of gray samples in this color target. The first set is the mixture of titanium white and carbon black whereas another set is a mixture of chromatic pigments to evaluate the accuracy of the spectral estimation for metameric pairs. This combination of color patches makes MCSL paint color target a perfect independent color target with reasonable spectral variations in wide
range of hue angles. The averaged camera responses of each color patch were used for the calculations.

![ColorChecker Passport with 24 matte samples.](image)

**Figure 3.12:** ColorChecker Passport with 24 matte samples.

![Munsell Color Science Laboratory Spectral Target 1](image)

**Figure 3.13:** The MCSL paint color target.

For evaluating the geometry effects, glossy color patches of a custom color target with were utilized. The custom color chart was comprised of 100 matte and glossy patches. Different patches were made by mixing Golden matte acrylic paints to achieve a reasonable color gamut, a set of neutral and dark patches, as shown in Figure 3.14. An automotive gloss coating was applied to half of the samples to generate the glossy surfaces (Figure 3.14). The dark patches are useful for evaluating the performance of spectral characterization where the measurement sensitivity is more critical. A Photo Research PR-655 SpectroScan tele-
spectroradiometer (PR-655) was used for the radiance measurements. The spectroradiometer was placed approximately at the same place as the acquisition camera. The reflectance factor of each patch was obtained using Polytetrafluoroethylene (PTFE) as the reference white. For all the color targets, the camera responses of each color patch were extracted by averaging the pixel values by considering approximately 50% of the sample area.

![Figure 3.14: The custom color chart with 100 glossy and matte patches under the light booth at specular angle. (a) 50 matte patches, (b) 50 glossy patches. The image at the left corresponds with the isotropic lighting. The image on the right shows the same color chart in the specular angle under the light booth for illustrating the difference between glossy and matte patches.](image)

3.2.2 Results and discussion

3.2.2.1 Angular Dependency Correction

The effect of filter transmittance shift for the red matte sheet is shown in Figure 3.15. Notice that the camera response changes toward the borders of the image due to the angular differences. The histogram of the image implies significant effect of the wavelength shift when the signal is normalized between zero and one. Ideally the camera responses must be similar for all pixels when no wavelength shift exists.
Figure 3.15: The non-uniformity of acquired data for red color sheet before correction (capturing channel corresponding to 611 nm). a) a pseudo image showing non-uniformity of the red patch before correction. b) is the histogram of the same image.

This angular dependency was quantified by calculating the color difference of each segment of the image to the center of the image for six uniform solid sheets. The captured image was segmented to 30×40 sections and the average value of each segment was compared to the central segment using CIEDE2000. The mean and maximum CIEDE2000 values of each segment are plotted in Figure 3.16 (a) and Figure 3.16 (b). The mean (max) CIEDE2000 of 0.95 (4.00) implies significant effect of angular changes in the LCTF-based system.
Figure 3.16: Mean (a) and maximum (b) CIEDE2000 for six color fields before the angular correction.

The result of angular correction for the same samples is shown in Figure 3.17 and Figure 3.18. The mean and maximum of CIEDE2000 values before and after angular correction are summarized in Table 3.1. The mean (max) CIEDE2000 reduced to 0.08 (0.47) after correction.

Figure 3.17: Non-uniformity of acquired data for red color field before correction (for the capturing channel)
Figure 3.18: Mean (left) and maximum (right) CIEDE2000 for six color fields after correction.

Table 3.1: Mean and Maximum CIEDE2000 of segmented images of six solid color fields before and after correction.

<table>
<thead>
<tr>
<th></th>
<th>Before Correction</th>
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<tr>
<td>Mean of</td>
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<td>Segments</td>
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<td>Max of</td>
<td>Mean</td>
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</tr>
<tr>
<td>Segments</td>
<td>Max</td>
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</tr>
</tbody>
</table>

Further evaluation of wavelength shift was carried out by imaging the ColorChecker Passport in five locations of the scene (Figure 3.19). CIELAB values of ColorChecker Passport were calculated for illuminant D65 and 1931 standard observer. The average CIEDE2000 values for 18 chromatic patches for five positions before and after angular correction are shown in Table 3.2 and Table 3.3. The gray samples were removed from the evaluation set because they are not affected by wavelength shift. The mean CIEDE2000 up to 1.82 expresses noticeable effect of the angular changes when the color checker is placed in two extreme corners of the scene, which reduced to 0.51 after angular correction.
Figure 3.19: Spectral capturing of ColorChecker Passport in five different location of the scene.

Table 3.2: the mean of CIEDE2000 values for chromatic patches of ColorChecker Passport in different locations of the scene before angular correction.

<table>
<thead>
<tr>
<th></th>
<th>Center</th>
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<th>Down Right</th>
<th>Down Left</th>
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<tr>
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<td>Up Right</td>
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<td>0.02</td>
<td><strong>1.82</strong></td>
<td>1.78</td>
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<tr>
<td>Up Left</td>
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<td>0.02</td>
<td>0.00</td>
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<tr>
<td>Down Right</td>
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<td>1.82</td>
<td>1.81</td>
<td>0.00</td>
<td>0.82</td>
</tr>
<tr>
<td>Down Left</td>
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<td>1.78</td>
<td>1.77</td>
<td>0.82</td>
<td>0.00</td>
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</table>

Table 3.3: the mean of CIEDE2000 values for chromatic patches of ColorChecker Passport in different locations of the scene after angular correction.

<table>
<thead>
<tr>
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<td>Up Left</td>
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<td>0.00</td>
<td><strong>0.51</strong></td>
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<tr>
<td>Down Right</td>
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<td>0.42</td>
<td>0.51</td>
<td>0.00</td>
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<td>Down Left</td>
<td>0.22</td>
<td>0.25</td>
<td>0.27</td>
<td>0.41</td>
<td>0.00</td>
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</table>
3.2.2.2 Spectral Characterization

The next step is to use the corrected camera responses for spectral reconstruction according to Eq. 3.7. As already mentioned, the $\beta$ values are optimized based on the spectral reflectances of 24 samples of ColorChecker Passport as the training data. The results of spectral imaging of the ColorChecker before and after characterization are shown in Figure 3.20. The colorimetric changes are also illustrated in Figure 3.21. The colorimetric values before characterization correspond to the raw spectral reflectance that derived from the camera without any correction. In this case the camera signals are treated as spectral reflectance values. Colorimetric and spectral comparisons of estimated and measured reflectances are shown in Figure 3.22. The results of CIEDE2000 values of the training color target for each characterization step are shown in Table 3.4. The mean (max) CIEDE2000 of 0.45 (1.06) is an acceptable level of perceptual match between the estimated and measured spectral reflectance factors. The mean RMS of 0.00446 (0.4%) also depicts a reasonable linear correlation between estimated and measured spectral reflectance factor, which is an important factor for pigment identification. According to the color differences in Table 3.4, the final spectral characterization led to a noticeable improvement to the estimations compared to a regular interpolation after flat-fielding.
Figure 3.20: ColorChecker Passport before (left) and after (right) characterization process.

Figure 3.21: CIELAB values of the ColorChecker Passport in CIELAB color space (a*, L* and C*) before and after applying characterization algorithm on the measured camera signals. In each plot, filled circles represent estimated values of the custom color chart. The line connected to each circle shows the location of the actual value measured by i1 spectrophotometer.
Figure 3.22: Actual (solid black) and estimated (dashed red) reflectance factors of the ColorChecker Passport patches. For each patch, the number at top-left corner indicates CIEDE2000 value between actual and predicted curves. The color of each sample is divided into two upper and lower triangles. The upper and lower triangles are rendered corresponded to the predicted and actual reflectance factors respectively.

Table 3.4: CIEDE2000 and spectral RMS values between actual (from spectrophotometer) and the estimated reflectance factor of the ColorChecker Passport (training dataset) according to different calibration and characterization step.

<table>
<thead>
<tr>
<th></th>
<th>CIEDE2000</th>
<th></th>
<th>Spectral RMS</th>
<th></th>
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<td>Mean</td>
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<td>Variance</td>
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<td>11.95</td>
<td>4.45</td>
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<tr>
<td>Dark Corrected</td>
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<td>12.01</td>
<td>4.33</td>
<td>10.19</td>
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<tr>
<td>Flare Corrected</td>
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<td>12.14</td>
<td>4.02</td>
<td>10.33</td>
</tr>
<tr>
<td>Flat Fielded</td>
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<td>2.24</td>
<td>0.34</td>
<td>1.95</td>
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<tr>
<td>Angular Corrected</td>
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<td>0.32</td>
<td>2.03</td>
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<tr>
<td>Flat Fielded</td>
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<td>2.11</td>
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<td>2.07</td>
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<td>Spectrally Characterized</td>
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<td><strong>1.06</strong></td>
<td><strong>0.06</strong></td>
<td><strong>0.91</strong></td>
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</tbody>
</table>

The MCSL paint color target was used as an independent dataset for validating the spectral imaging system. The estimated and measured spectral reflectance factors are plotted in Figure 3.23. The mean (max) CIEDE2000 and RMS values are 0.4 (1.7) and 0.77% (2.5%). Similarity of color differences of training and independent color targets indicates that the characterization did not overfit to the test data. In other words, the characterization process is independent of the color target. The average CIEDE2000 and RMS for estimated spectral factor for the test color target are shown in Table 3.5. The results also emphasize the importance of the spectral
characterization step compared to simple interpolation on flat-fielded images. If the flare and wavelength correction are omitted from the characterization workflow the average (max) CIEDE2000 and RMS values increases to 0.7 (1.8) and 0.96% (3.0%), respectively. For more details of the effect of each calibration and characterization step are see Appendix C.

Table 3.5: CIEDE2000 and spectral RMS values between actual (from spectrophotometer) and the estimated reflectance factor of the MCSL paint color target (independent dataset) according to different calibration and characterization step.

<table>
<thead>
<tr>
<th></th>
<th>CIEDE2000</th>
<th>Spectral RMS</th>
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</thead>
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<tr>
<td>Spectrally Characterized</td>
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<td><strong>1.65</strong></td>
</tr>
</tbody>
</table>
3.2.2.3 Geometry Dependency

The experiment was carried out using 50 glossy patches of the custom color target shown in Figure 3.14. The spectral data were corrected according to Eq. 3.5 for geometry dissimilarity and compared to those from a PR-655 spectroradiometer. Consequently, spectral reflectances from spectroradiometer and spectrophotometer were related using the Berns-Petersen method with an offset. For geometry correction, the calculated offsets ($\rho$ in Eq. 3.5 or $\beta$ in Eq. 3.7) were omitted and then corrected for the reference white (for obtaining $\mu$ in Eq. 3.5). Note that $\mu$ is a single scalar that will be optimized according to all the reflectances of the PTFE for the camera taking geometry. Eventually, the geometry corrected model results in a correct estimation for PTFE after offset removal. The training dataset and characterization workflow was kept the same as previous experiments except the geometric correction was added to the characterization process. The results are shown in Table 3.6 and Figure 3.24. The average CIEDE2000 was improved from 1.5 to 0.8 after geometry correction. The average and maximum RMS values are similar to the results from the independent color target (mean and maximum of 0.6% and 2.0%). The results of the spectral predictions before and after geometry correction are illustrated in Figure 3.24. The improvements mostly involved dark samples, which are more sensitive to geometry differences. The results point out that the geometry-corrected spectral characterization is still valid for other sorts of materials and is independent of the surface structure. The third row of Table 3.6 (self Trained) shows the error values when 50 glossy samples of the custom color target are used for training and testing as ground truth. It should be noted that a part of the error is due to the dark samples with small SNR. The slight geometry difference between the multispectral camera and spectroradiometer measurement can also be another source so of error after geometry corrections. See Appendix D for further analysis of the methods.
Table 3.6: CIEDE2000 and spectral RMS values between actual (from spectrophotometer) and the estimated reflectance factor of the 50 glossy samples of a custom color target for before and after geometry correction.

<table>
<thead>
<tr>
<th></th>
<th>CIEDE2000</th>
<th>Spectral RMS</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>Max</td>
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<td>Regular Characterization</td>
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<tr>
<td>Geometry Corrected</td>
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<td>2.63</td>
</tr>
<tr>
<td>Self Trained</td>
<td>0.60</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Figure 3.24: CIELC plots of the custom color chart patches calculated from actual (measured by spectroradiometer) and estimated reflectance factor before (a) and after (b) geometry correction.

3.3 Measuring Paintings

The spectral images of 30 paintings were collected using incandescent light sources (Elinchrom Scanlite Digital 1000) to reduce the measurement sensitivity to temporal instabilities of the Xenon light sources caused by the temperature and humidity changes. The SPD of the HMI light sources plotted in Figure 3.25. Note that small variations in light source SPD can lead to noisy curve shapes after spectral reconstruction. However, replacing the light sources coincided with a new geometry changes, such as more optical blurriness to the images and lower emitted energy for short wavelength. It also necessitated an efficient cooling system to control the temperature increase caused by the tungsten lights.
A colorimetric rendering as well as the pigment information of the paintings are shown in Appendix E. The spectral images were processed for dark current, flare, flat fielding and angular dependency. The capturing geometry was converted to the capturing geometry of the ColorEye XTH spectrophotometer since it had been used for spectral measurements of the pigment database explained in Ref. (Okumura, 2005). The geometry conversion was based on gray samples of the ColorChecker Passport using Eq. 3.5.

**3.4 Conclusions**

A practical workflow for characterizing an LCTF-based multi-spectral acquisition system was introduced. The characterization workflow was based on a set of standard samples with known reflectance factor provided by a spectrophotometer.

A surface correction method based on the Saunderson equation was selected and applied to the spectral data of the training data set to compensate for geometrical dissimilarities between camera responses and reflectance factor data measured by spectrophotometers. The Saunderson equation has the advantage of simplicity and applicability for isotropic paint surfaces compared to the variety of available models. The influence of the Saunderson correction was assessed by comparing spectrophotometric and spectroradiometric measurements. The correlation of the
reflectance factor data from two spectrophotometers and a spectroradiometer was studied in three lighting geometries. The results validated that the Saunderson correction method was capable of compensating for reflectance changes due to lighting geometries. In addition, a simplified version of the Saunderson equation was also implemented and evaluated, assuming similarity in the internal reflection coefficient for different geometries. The trivial differences between Saunderson and the simplified form of the equation confirmed the validity of this assumption for paint surfaces.

Afterward, a spectral reconstruction was carried out on dark corrected, linearized signal after an LCTF angular non-uniformity correction. The LCTF angular correction was performed based on a special correction for a set of matte solid color sheets by segmenting the image and using the Berns-Petersen spectral correction method. Corrected camera responses were used for deriving the spectral characterization parameters based on a training dataset. The spectral characterization was also based on the Bern-Petersen spectral correction for each capturing band. The characterization process was evaluated using two independent color targets. The first color target comprised of 54 matte color patches for evaluating the performance of the spectral characterization procedure. According to the results, characterization led to reasonable estimations accuracy and precision. In addition, the results verified that the ColorChecker Passport contained enough samples for describing the spectral properties of the capturing system. The geometry dependency of the characterization was assessed by comparing the estimated reflectance factors of 50 glossy patches to those measured by a spectroradiometer.

Small CIEDE2000 and RMS values of the estimation indicate that the proposed method provided accurate enough data for pigment identifications goals. The geometry independency of the model is applicable when the paining does not have the same surface property as the training color target.
CHAPTER 4: A LINEAR COLOR MIXING MODEL FOR ARTIST PAINTINGS

Development of a pigment identification (PI) pipeline relies on a linear subtractive mixing model. Of the available subtractive mixing theories, Kubelka-Munk (KM) describes the interaction of light and a medium through a simple, but non-linear, set of equations for limited forms of matter and lighting geometries. Kubelka-Munk theory has been used for analysis, treatment, and conservation of paint layers in museums, but only for spot measurements. As a new application of KM theory, its functionality requires more exclusive evaluation for image-based pigment identification. The linearity requirement leads to the single-constant KM (1-KM) theory as a linear derivation of the general KM theory; however, its application is restricted to highly scattering mixtures. Verification of KM theory for characterizing paint layers as well as developing a linear form of the theory for PIs are discussed in this chapter. First, the performance of KM theory is evaluated using two sets of mixture databases. Next, the results are extended for 1-KM for linearity assessment. Finally, the relationship of 1-KM and dimensionality reduction algorithms is examined for PI using linear unmixing models.
4.1 Verification of 2-KM for PI

In spectral-image-based PI algorithms, a large number of paint mixtures with wide concentration ranges are used for primary extractions. Consequently, the efficiency of the KM theory for different pigment concentrations becomes a key factor for PI. Ultimately, a confident region of pigment concentration in which the KM theory yields accurate estimations is determined. The evaluations mostly focus on the dark and high-saturated mixtures where KM theory produces poor estimations.

According to the KM theory, the spectral properties of any mixture are characterized using optical properties of the primary pigments. Traditionally, the optical information of the primary pigments is extracted using a set of binary mixtures of the chromatic component and white. For PI, the optical coefficients of the primary pigments are derived according to a set of spectral data depending on the painting's contents. An appropriate selection of training data that results in a reasonable estimation for primary elements facilitates the process of PI, which is investigated in this section. Accordingly, a set of experiments was carried out to evaluate the performance of KM theory for a variety of artists' pigments, concentration ranges, and training mixtures. Experiments were conducted for individual and multiple mixtures of pigments.

4.1.1 Experimental

The evaluations were carried out in two parts using two sets of pigment mixtures: 1) binary mixtures comprised of 28 chromatic pigments and a white component for preliminary assessments and 2) a database of 126 mixtures consisting of combinations of three chromatic pigments for a set of testing and training mixtures.

The training sets were evaluated by calculating RMS errors of estimated K/S curves, concentrations, spectral reflectance, and CIEDE2000. Meanwhile, K/S and concentration predictions are considered as key metrics since they specify the validity of KM theory. The CIEDE2000 and RMS error of estimations are listed in Appendix F. The workflow of K/S estimation and error calculations is shown in
Figure 4.1. All of the spectral reflectances were corrected for surface refractive index discontinuity using the Saunderson equation. Unit k and s coefficients were extracted relative to the white component using a least squares method (Walowit, et al., 1987).

4.1.1.1 Part I: Binary Mixtures

The optical properties of 28 Golden matte artist acrylic dispersion paints, available in Okumura's pigment database (Okumura, 2005), were extracted according to different training sets. The database contains a variety of pigments with a wide range of scattering and absorption properties covering three pigment categories introduced by Johnston-Feller (2001). Type I pigments refer to those with a high amount of scattering, such as titanium white; type II pigments are those with a high amount of absorption (mostly organic), such as carbon black, phthalocyanine blue, carbazole dioxazine violet, and phthalocyanine green; and type III pigments have significant scattering and absorption properties, such as molybdate orange and light chrome yellow. Considering this definition, 1-KM is a proper model for type II pigments when the concentrations are not extreme. For type III pigments, both
scattering and absorption are effective; therefore, the scattering and absorption of the pigment should be specified for spectral estimations, which can be accomplished with 2-KM theory.

The database is comprised of several concentrations of the pigments with titanium white drawn down on black and white substrate to insure opaque paint layers. Four or five drawdowns were made for each pigment with respect to the strength of the colorant. The spectral reflectance of the opaque layers was measured by a GretagMacbeth Color Eye XTH spectrophotometer with integrating sphere and specular component included ($di:8^\circ$), providing diffuse lighting suitable for KM theory to be valid. The CIE tristimulus and CIELAB values were calculated for the 1931 standard observer and illuminant D65. The Saunderson correction was applied ($k_1=0.03$, $k_2=0.65$) to transform the measured reflectance factor to the internal reflectance as explained by Okumura (2005).

4.1.1.2 Part II: Mixtures of Pigments

Three chromatic pigments (hansa yellow Opaque PY74, quinacridone magenta PR122, phthalo blue PB15:4, with titanium white PW6) were selected from the pigment database, and the optical properties were calculated using different training datasets. Selected pigments have dissimilar types of optical properties to cover all three types of pigments. Titanium white is a Type I pigment; phthalo blue and hansa yellow are Type II and Type III, pigments respectively. Quinacridone magenta is a Type II pigment with a large amount of absorption, but not as much as Phthalo Blue. It is important to mention that making opaque drawdowns for both type II and type III pigments can be difficult, depending on the proportion of the pure pigment in the resin. The issue of making opaque layers is more noticeable in mixtures with high pigment concentrations and masstones.

The database is comprised of 126 concentrations of the pigments with titanium white paint drawn down on the black and white substrate to obtain opaque paint layers. The pigment proportions of the 126 mixtures using three chromatic
pigments are shown in Figure 4.2. The mixtures of pigments were prepared with caution to make uniform and smooth layers of paint. To obtain opacity, necessary numbers of paints layers were made on top of previous dried layers. It should be noted that applying thick layers of paint were not desirable due to the problem of surface bubbles. The drawdowns were done by a byko-drive automatic film applicator (Figure 4.3).

![Figure 4.2: The concentration ratios of mixing three chromatic pigments (hansa yellow, quinacridone Magenta, phthalo blue) with titanium white to make 126 opaque drawdowns.](image)

![Figure 4.3: (a) Three chromatic pigments (hansa yellow Opaque PY74, quinacridone magenta PR122, phthalo Blue PB15:4, with titanium white PW6) from Golden matte artist acrylic paints. (b) byko-drive automatic film applicator. (c) A view of the 126 drawdowns on the drying rack.](image)

The database was divided into different types of mixtures shown in Figure 4.4. In this figure, *Tint Ladders* refer to the binary mixtures of each pigment and white. *Masstones* are the pure pigments with no titanium white. For Tint Ladders, nine
concentrations of each pigment and white were made to have finer intervals. A non-linear concentration ratio was selected for finer concentration intervals near the extreme ranges. The chosen pigment concentrations for the Tint Ladder of an individual pigment are shown in Figure 4.5. The Tenth mixture in this figure is the masstone with the concentration of unity. Tints are defined as mixtures with a reasonable amount of chroma when they are mixed with titanium white (Berns, and Mohammadi, 2007). Saturated mixtures refer to the mixtures of pigments with a very small amount of titanium white (pigment concentration of 95% and 5% titanium white). Therefore, Saturated-Tint mixtures are rather similar to Masstone-Tint mixtures, except that the masstones are replaced with a saturated mixture. Binary mixtures are sets of mixtures made by mixing two chromatic pigments plus white.
Figure 4.4: The schematic illustration of the database comprised of 126 mixtures. Each circle demonstrates a mixture of three chromatic pigments and titanium white. The concentration of each component is simulated by the area of each one of the primary pigments in the figure. The outer circle simulates the actual color of each mixture.
Figure 4.5: The pigment concentrations of the Tint Ladder comprised of ten mixtures.

The spectral reflectance of the opaque layers was measured by a GretagMacbeth Color Eye 7000 integrating sphere spectrophotometer and specular component included (di:8°) providing a diffuse lighting suitable for KM theory. Saunderson coefficients, $k_1$ and $k_2$ were optimized and set to 0.030 and 0.537.

The spectral reflectance and a*b* plots of the samples are shown in Figure 4.6 and Figure 4.7. CIE tristimulus and CIELAB values were calculated for standard observer 1931 and D65 illuminant for calculating perceptual color differences using CIEDE2000.
The KM coefficients were estimated using different sections of the database as the training dataset according to Table 4.1. The list of validation datasets is also shown in Table 4.2 and minimizing the RMS errors of K/S curves for all three pigments simultaneously as opposed to the conventional methods in which each pigments is characterized independently. Tint ladders were examined in a separate step since they are common training datasets in practice.
Table 4.1: Training Datasets.

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<th>Training Datasets</th>
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<tr>
<td>Tint Ladders No Masstones</td>
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<tr>
<td>Masstone Tint Method</td>
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<tr>
<td>All Mixtures No Masstones</td>
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</tr>
<tr>
<td>All Mixtures</td>
<td>126</td>
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<tr>
<td>Binary Mixtures</td>
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<tr>
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<tr>
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<tr>
<td>Saturated Tint From Binary Mixtures</td>
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<tr>
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Table 4.2: Validating Datasets.

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</thead>
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<td>Tint Ladders No Masstones</td>
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<td>All Masstones</td>
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<td>Same as Training</td>
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4.1.2 Results and Discussion

4.1.2.1 Part I: Binary Mixtures

The KM theory was evaluated using binary mixtures of 28 chromatic pigments and white. The following section discusses the effect of the training set on the KM predictions.

4.1.2.1.1 Tint ladder with no masstones in the training data

In this section, masstones were removed from the training dataset; however, the testing datasets include both tint ladders with and without masstones. The RMS values of K/S curves are shown in Figure 4.8 in linear and log scales. The log scale provides more details of the estimation error when errors values have a large range.
Figure 4.8: The mean RMS errors of actual and estimated K/S for 28 pigments. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error. The lines and open circles in the log scale plot are the 90th percentile and maximum error respectively.
Basically, large errors belong to the masstones of type II pigments (such as ultramarine blue and quinacridone magenta) with a small amount of scattering. Pigments with high scattering coefficients, such as yellow ochre or red oxide, led to smaller prediction errors for masstones. An example of the K/S curves of ultramarine blue pigments is shown in Figure 4.9. The normalized K/S curves depict how the general K/S shapes lose their scalability for dark mixtures and masstones. The differences in spectral shape explain the large error of estimating the masstones when they are not in the training dataset. These changes of the spectral shape have already been reported as a behavior of type II pigments in their pure form (Johnston-Feller, 2001). Unfortunately, the actual behavior of the K/S could not be studied more exclusively due to the large concentration intervals of Okumura’s pigment database. A finer concentration interval in the second experiment, however, allowed further evaluations of dark mixtures described in the next section.

![Figure 4.9: Actual (left) and normalized to maximum (right) K/S curves of ultramarine blue ramps and the masstone from the database of 28 artist paint.](image)

The CIELAB coordinates of actual and estimated curves are plotted in Figure 4.10. Generally, the KM theory produced accurate results for the light and medium shades. The large errors correspond to the dark shades, including masstones and mixtures with high pigment concentrations.
4.1.2.1.2 Tint ladder with masstones in the training data

The K/S RMS errors of the estimations are shown in Figure 4.11. An obvious advantage of adding masstones to the training is the prediction improvements for dark mixtures. Meanwhile, K/S RMS errors did not increase significantly for the tint ladders. It can be concluded that adding the masstones into the training dataset provide spectral variations useful for characterizing dark mixtures. On the other hand, the light ramps can still be characterized by rectifying the remaining degree of freedom of the k and s coefficients. The prediction improvement also can be seen in the CIELAB plot (Figure 4.12).
Figure 4.11: The mean RMS errors of actual and estimated K/S for 27 pigments. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error. The lines and open circles in the log scale plot are the 90th percentile and maximum error, respectively.
Figure 4.12: CIELAB L*-C* plot of actual (filled circles) and (lines) predicted samples of 126 pigments concentrations.

Note that the measurement noise is more significant when dark masstones are involved. The K/S curve of the ultramarine blue masstone is noisy with large quantities (Figure 4.33). The large (K/S) values severely affect the k and s coefficient estimations when least-squares methods are used in (K/S) space. The scattering coefficient of the ultramarine blue highlights the effects of measurement noise for masstones (Figure 4.13).

Figure 4.13: Scattering coefficient of ultramarine blue pigment using 2-KM method.
The presence of masstones to the training dataset slightly decreases the prediction accuracy for other mixtures. The results of K/S RMS values of the validation set without the masstones are shown in Figure 4.14. Comparing different training datasets, the prediction errors of the training dataset without masstones are smaller. The spectral reflectance, CIEDE2000, and concentration RMS plots can be found in Appendices F and G. The influence of the masstones on the predictions is statistically significant. A t-test (95% significance level) on the RMS values for all the mixtures with different test and training datasets also confirms a significant increase of CIEDE2000, K/S, and reflectance RMS errors when masstones are involved with the testing or training sets. The concentration RMS errors, however, are not significant statistically.
Figure 4.14: The mean RMS errors of actual and estimated K/S for 28 pigments when masstones are removed from validation set. The plot illustrates the prediction with training sets with (bottom) and without (top) masstones. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error.
4.1.2.2 Part II: Mixtures of Pigments

The performance of the KM theory when the training data was comprised of multiple combinations of primary pigments was studied in this section. Therefore, the evaluations are based on combinations of three chromatic primary pigments.

4.1.2.2.1 Tint Ladders

The new dataset provides finer sampling for different concentration ratios, which enables deeper examination of the KM theory specifically when the proportion of the white element is very small.

The reflectance and K/S curves for tint ladders of three pigments are shown in Figure 4.15. The spectral and K/S plots of the mixtures depict how three pigments behave differently by varying concentration ranges. Also, the curve shapes indicate rather high K/S values for dark masstones, which implies a significant influence of masstones on the estimated KM and Saunderson coefficients. Meanwhile, the measurement noise is higher for masstones due to the small reflectance values.

The normalized K/S curves of the tint ladders are a useful way of studying the scalability of the curves (Figure 4.16). For type II pigments (hansa yellow and quinacridone magenta), the K/S curves can be divided into two sections. The first concentration region contains K/S curves representing light-shades (tint-ladders 1-
4) and scalable mixtures when the scattering component is dominant (see normalized K/S curves of phthalo blue pigment in Figure 4.16). This range of concentration is an accurate region for applying 1-KM theory (Davidson, et al., 1963; Davidson, and Hemmendinger, 1966). The second region includes mixtures with the K/S curves that do not follow scalability as the pigment concentration increases. Clearly, the deviation from the scalability occurs gradually when the pigment concentration gets close to unity. As a result, the scalability violation is particularly limited to the masstones but also dark and saturated mixtures.
Figure 4.16: The normalized K/S values for tint ladders of three chromatic pigments and masstones. The K/S values are normalized to K/S value at the wavelength with the maximum K/S for each pigment.

For an exclusive evaluation of the training data, tint ladders with different numbers of mixtures were examined. The number of mixture concentrations started from five mixtures with the lowest pigment concentrations. More light mixtures were added
to the tint ladders sequentially until there were 10 mixtures for each training set. The results were compared to the masstone-tint and saturated-tint training datasets, where only two mixtures per pigment is recommended. The K/S RMS errors associated with different tint ladders and testing datasets are shown in Figure 4.17. In this figure, Light Tint Ladders 1-n refer to a tint ladders comprised of the first lightest n-th mixtures. For instance, Light Tint Ladder 1-5 includes five mixtures with the lowest concentrations for each pigment. See Appendix H for the results of average CIEDE2000, concentration RMS, and spectral reflectance RMS errors for similar training and validation datasets.

Figure 4.17: The mean RMS errors of actual and estimated K/S for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refers to the total number of samples in each dataset. The filled circles represent the median of the error.
Considering Figure 4.17, RMS errors corresponding to the masstones are relatively large regardless of the training data. The errors imply poor predictions of KM theory for dark masstones even when the masstones are in the training dataset. Including masstones for calculating KM (and Saunderson), coefficients might lead to significant improvement for dark mixtures, but it slightly increased the prediction errors for lighter mixtures. Figure 4.18 is a demonstration of KM performance when the tint ladders of three pigments with and without masstones in the training datasets. Including masstones into the training database enhanced the predictions for dark mixtures, although the masstones generated larger errors for light and medium shades.
Figure 4.18: CIELAB L*-C* plots of actual and predicted samples of all the mixtures (126 samples) for the tint ladders with (a) and without (b) masstones as training data.

The training set comprised of tint ladders with light mixtures also yields larger estimation errors compared to the other training datasets. Using light mixtures for coefficient estimations of 2-KM theory leads to underdetermined sets of equations, since the K/S curves can be characterized by a single basis function. In other words,
light mixtures do not deliver sufficient fluctuations for dark mixtures. Single-
constant KM (1-KM) can be as effective as 2-KM theory for light mixtures. As a
result, the tint ladder must include at least one sample outside of the scalable region
to predict darker mixtures. The performances of the tint ladders that contain one or
more samples in second concentration regions are rather similar and equivalent to
the masstone-tint or saturated-tint training dataset. Considering Figure 4.17,.masstone-tint and saturated-tint methods led to rather similar results in the
spectral matching of 126 patches; therefore, there is no advantage of saturated
mixtures over masstones in the masstone-tint method. In addition, using masstone-
tint method led to similar estimations as a full ramp tint ladder (with all mixtures),
even though KM theory is not valid for masstones.

The results confirm the masstone-tint method proposed by Berns and Mohammadi
(Berns, and Mohammadi, 2007) for estimating KM coefficients with only two
mixtures as a training dataset. This approach provides simplicity in calculations and
performance in estimations. According to the results, Berns and Mohammadi’s
method has maintained its validity despite the weakness of the theory in
classifying dark mixtures.

4.1.2.2.2 The Mixture Combinations

For PI, the optical properties of the pigments are specified using a set of pigment
mixtures in contrast to the conventional methods of using independent ramps. The
RMS errors of different training sets against a variety of validation sets are shown in
Figure 4.19 and Figure 4.20. Other than masstones, the prediction accuracy of K/S
curves is rather similar for all of the methods. In general, adding more samples to
the training dataset did not change the results significantly. The estimation for
masstones still contains large errors even when masstones are part of the training
dataset.

Looking at spectral RMS errors and CIEDE2000, the predictions are better for tint-
ladder-based training datasets (Figure 4.20). In some instances, complex mixtures
into the training data led to a non-realistic spectral shape for estimated reflectances. This is mainly due to the negative values in K/S space. For example, when the spectral reflectance of tint ladders comprised of all mixtures were used as the training data, estimations turned spiky due to the high degree of freedom and negativity of K/S in some wavelengths at the optimization process, which affects the estimations in the wavelengths with very small K/S. This problem is shown in Figure 4.21. This figure is a plot of estimated spectral reflectances of the tint ladders when all the 126 mixtures are used for training, which is a common case in IPs. Notice large errors corresponds large spectral reflectance with small K/S. The results confirmed the inefficient perceptual estimations when K/S curves are matched.

Figure 4.19: The mean RMS errors of actual and estimated K/S for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refers to the total number of samples in each dataset. The lines and the filled dots show the 90th percentile and median of the errors, respectively.
Figure 4.20: The mean RMS errors of actual and estimated spectral reflectance (a) and CIEDE2000 (b) for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refers to the total number of samples in each dataset. The lines and the filled dots show the 90th percentile and median of the errors, respectively.
Adding perceptual terms to the optimization procedure is one remedy to the abovementioned problem. Minimizing RMS errors in K/S space does not essentially generate appropriate perceptual outcomes; therefore, incorporating spectral reflectance- or colorimetric-based metrics can enhance the perceptual aspects of the estimations. One approach is to replace the regression (or matrix pseudo inverse) methods with a non-linear optimization method. The results from regression algorithm are utilized as proper starting values. The optimization process can be designed as plotted in Figure 4.22. The workflow provides a refinement step for unit k and s as well as concentration estimations. The pigment concentrations are updated using regular regression methods based on the new coefficient estimations. The estimated values of regular regression methods are used as starting values for minimizing RMS errors of spectral reflectance. The spectral reflectance-based refinements, particularly addressed the spectral estimations with the small K/S values. An example of the spectral reflectance estimations is shown in Figure 4.23. The spectral predictions in Figure 4.23 are the corrected form of the same sets of patches shown in Figure 4.21. The improvements specifically smooth the regions with small K/S values. Unfortunately, this method cannot be considered as an empirical solution for pigment identification algorithms due to complexity and processing time.
Another practical alternative for improving the KM estimations is to apply perceptual weighting functions to the least squares solution. The weighting function
eventually intensifies the RMS errors for the larger spectral reflectances in the regression process. The formulation can be written as follows (McDonald, 1997):

\[
\begin{bmatrix}
w_j \frac{K}{S}_{mix,j}
\end{bmatrix} = \begin{bmatrix}
w_j \sum_{i=1}^{n} c_{i,j} k_i
\end{bmatrix}
\]

Eq. 4.1

In this formula, \( w_j \) is a weighting coefficient corresponding to the j-th mixture; \( k \) and \( s \) are unit KM absorption and scattering coefficients, and \( c \) is the concentration or the portion of each component. Subscript \( i \) denotes the contribution of the \( i \)-th primary pigment. The weighting value, \( w_j \), can be easily written for driving either the unit \( k \) and \( s \) or the pigment concentrations, \( c_i \).

A weighting factor corresponding to the spectral reflectance of the mixtures as function of wavelength \( (w_{\lambda,i} = R_{\lambda,i}) \) was found to be a reasonable weighting coefficient compared to that recommended in Ref. (McDonald, 1997), which is the inverse of the derivative of Eq. 2.51 \( (w_{\lambda,i} = 2R_{\lambda,i}^2/(1-R_i^2)) \). The result of spectral reconstruction using the weighting function is shown in Figure 4.24. The results are comparable to those from the previous section with non-linear optimization. The improvement of CIEDE2000 and spectral reflectance RMS can be observed in Figure 4.25.

Figure 4.24: Estimated (solid lines) and actual (dashed lines) of spectral reflectance of tint ladders when all mixtures are used as training data after refinement by minimizing RMS errors of \((K/S)\) curves with weighting function.
Figure 4.25: The mean RMS errors of actual and estimated spectral reflectance (a) and CIEDE2000 (b) for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refers to the total number of samples in each dataset. The lines and the filled dots show the 90th percentile and median of the errors, respectively.
4.1.2.2.3 The Concentration Estimations

Concentration estimation is a substantial aspect of KM theory for color-matching recipe predictions. The concentration RMS errors associated with different training and validation datasets are plotted in Figure 4.26. According to the results, the concentration estimations improve by adding binary or triple mixtures to the training data. Using tint-ladder and masstone tint based methods produced larger estimation errors specifically for masstones. The unit k and s coefficients calculated using different training dataset are plotted in Figure 4.27.

Figure 4.26: The mean RMS errors concentration estimations for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refers to the total number of samples in each dataset. The lines and the filled dots show the 90th percentile and median of the errors respectively.
The predicted coefficients differ in their scattering coefficients. The differences between scattering coefficients can be due to the interaction between pigments. Adding triple pigment mixtures is the most effective factor improving the estimations. The CIELAB L*-C* plots of actual and estimated patches are the same reason (Figure 4.28 and Figure 4.29). These figures are better perceptual illustrations of colorimetric differences. The use of all the mixtures for training
particularly enhanced the predictions of the green patches (Figure 4.29). A possible reason is the dissimilarities of KM coefficients for complex pigment mixtures compared to the tint ladders. It should be noted that inaccurate concentration estimations of 2-KM theory is a common problem in practical color matching procedures, which is addressed by a separate step called batch correction (McDonald, 1997).

Figure 4.28: CIELAB L*-C* plots of actual and predicted samples of all the mixtures for a)126 samples and b)18 samples of the masstones. Tint ladders with masstones are used as training data.
Figure 4.29: CIELAB L*-C* plots of actual and predicted samples of all the mixtures for a) 126 samples and b) 18 samples of the masstones. All 126 samples are used as training data.

4.1.2.2.4 Separate training database for different concentrations

An alternative for improving the predictions is to use piecewise training sets for light and dark mixtures. Thus, the training set is divided into two pieces for light and dark mixtures. The datasets consists of the five lightest and five darkest patches from the tint ladders for each pigment. The prediction results of estimations in
CIELAB $L^*-C^*$ color space are shown in Figure 4.30. The light training dataset yields excellent results but only for a limited number of light samples. As already explained, this dataset leads to large errors for masstones and darker mixtures. Instead, the dark dataset produces better results for almost all the testing datasets. Both the dark and light training datasets do not show a noticeable advantage over the other datasets, but the estimations for the dark mixtures improved slightly compared to the tint-ladder based training datasets.

Figure 4.30: CIELAB $L^*-C^*$ plots of actual and predicted samples of all the mixtures (126 samples) using (a) dark samples (b) light samples as training data.
4.2 KM Theory for Pigment Identification

In spectral-image-based pigment identification algorithms, primary pigments are extracted according to the spectral information of the available mixtures where both primary pigments and mixture concentrations are unknown. A viable piece of any pigment identification workflow is the validity of the subtractive model when characterizing pigment mixtures. Considering KM theory as the selected subtractive mixing model, it is important to evaluate its performance for describing the mixture’s behavior. According to the results, the estimations of K/S curves, spectral reflectance, and concentrations are not reliable for masstones and dark mixtures. The lower SNR of the measurements also intensifies poor predictions for the masstones. Accordingly, it is recommended to either remove or reduce the weight of the masstones and dark mixtures for pigment identifications unless more accurate subtractive mixing theories are used. The final pigment identification algorithm should be designed according to the performance of the KM theory for light and dark mixtures.

4.3 Verification of 1-KM for PI

The majority of available unmixing algorithms are developed, improved, and evaluated for linear mixing models (LLMs). Similar workflows are applicable for pigment PIs as long as the subtractive mixing model acts linearly. This consideration puts the single-constant simplification of KM (1-KM) theory as the first choice for subtractive mixing model due to its linearity, simplicity and inexpensive computations.

The 1-KM theory has been found to be applicable in textile and paper industries whereby the concentration of color pigment is small compared to the white substrate. Unfortunately, the 1-KM theory does not provide a perfect linearity for the paint layers since the presumed assumptions are not met (Billmeyer, et al., 1973b; Berns, and Mohammadi, 2007). This deviation causes some errors in pigment predictions and analysis, as mentioned in previous research (Berns, and Imai, 2002; Berns, et al., 2002; Zhao, et al., 2008).
The 1-KM theory can be modified to have better estimations for paint layers. In this section, a modified version of 1-KM is introduced that extends the functionality of 1-KM theory for a wider range of concentrations for paint layers. The modification exclusively addresses the systematic error of the 1-KM for concentration estimations.

4.3.1 Theory

The weaknesses of the 1-KM theory in concentration estimations can be addressed by formulating the scattering of the pigments rather than simply neglecting them. This implementation expands the applicable range of 1-KM theory for high scattering pigments. The scattering of each one of the components (\(s_i\) in Eq. 2.54) is assumed to be a portion of the scattered white component or \(p_is_w\). The new term, \(p\), is called the *impurity index* since it specifies the ratio of the white component co-operating as the scattering component in other colored pigments. Meanwhile, the linearity of the system is preserved beneficially for spectral image processing. It will be shown that this simple assumption enhances the concentration estimations compared to the 1-KM theory. According to this assumption, 2-KM theory (Eq. 2.54) can be written as follows:

\[
\left(\frac{K}{S}\right)_{mix} = \frac{c_wk_w + \sum_{i=1}^{n} c_i k_i}{c_w s_w + \sum_{i=1}^{n} c_i p_i s_w} \tag{Eq. 4.2}
\]

subject to \(\sum_{i=1}^{n} c_i + c_w = 1\). This equation can also be rewritten as:

\[
\left(\frac{K}{S}\right)_{mix} = \left(\frac{c_w}{c_w + \sum_{i=1}^{n} (c_i p_i)}\right) \left(\frac{k}{s}\right)_w + \sum_{i=1}^{n} \left(\frac{c_i}{c_w + \sum_{i=1}^{n} (c_i p_i)}\right) \left(\frac{k_i}{s_w}\right) \tag{Eq. 4.3}
\]

Comparing Eq. 4.3 and Eq. 2.56, the coefficient of unit \((k/s)\) values are corrected by incorporating the impurity index in the denominator of white and chromatic \((K/S)\) basis functions. The impurity term compensates for systematic errors of concentration estimations for high-scattering pigments and high pigment concentrations. The equation above also depicts that the new modification still maintains linearity and scalability characteristics in the \((K/S)\) space. As opposed to
the 1-KM model, if the concentration of the white component moves toward zero, the \((k/s)_w\) remains in the equation and prevents the denominator from getting close to zero eliminating the limitations of pure elements or masstons. Comparison of \((k/s)\) coefficients of Eq. 4.2 and Eq. 2.54 shows how the scattering of the pigments can deviate from the actual concentrations from those estimated by 1-KM theory. Conventionally, this estimation mismatch is compensated by numerical methods, such as 1D-LUTs, to map the actual and estimated concentrations of the ramps (see chapter 5 of Ref. (McDonald, 1997)).

In order to predict the spectral reflectance of a mixture, the relative absorption for each wavelength, as well as the impurity index, needs to be specified for each colorant. By extracting the relative absorption (also shown with \(\left(\frac{k}{s}\right)_w\)), and the *impurity index* \((p)\), the spectral reflectance of the mixture can be calculated similar to 2-KM theory. Setting the scattering of each pigment to a constant non-selective scattering of \(p\) for the entire wavelengths, the original form of the theory, Eq. 2.55, can be used alternatively.

In summary, the new method is a combination of both 1- and 2-KM theories, and inherits remarkable advantages from both by characterizing the scattering of the chromatic pigments in a linear space. These characteristics make this method a more appropriate choice for the analysis of the spectral images of the paintings, such as pigment identification and concentration maps.

### 4.3.1.1 Calculation of Coefficients

Calculating KM coefficients for the proposed method differs slightly from typical methods for 1- and 2- KM (Walowit, et al., 1987; Völz, 1995; Zhao, and Berns, 2009) because the impurity index is not independent of wavelength. Instead, it must be optimized for all wavelengths and concentrations, simultaneously using large sparse matrices. In order to optimize \((k/s_w)\) and the impurity index for each of the
pigments, Eq. 4.2 is written for mixtures of pigments with the white component (for
simplicity, \( \frac{k}{s} \) is denoted as \( \frac{k}{s} \) hereafter):

\[
\left( \frac{K}{S} \right)_{rmp,i,\lambda} = \frac{c_w \left( \frac{k}{s} \right)_{w,\lambda} + c_i \left( \frac{k}{s} \right)_{i,\lambda}}{c_w + c_i p_i}
\]

Eq. 4.4

\[
c_i \left( \frac{K}{S} \right)_{rmp,i,\lambda} p_j - c_i \left( \frac{k}{s} \right)_{i,\lambda} = c_w \left( \frac{k}{s} \right)_{w,\lambda} - c_w \left( \frac{K}{S} \right)_{rmp,i,\lambda}
\]

Eq. 4.5

where subscript \( rmp \) refers to a series of mixtures of the pigment and white
component with different concentrations, also known as tint-ladder. The equations
can be expanded easily when the ramp also includes black pigment in the mixtures.
To solve this equation for all concentrations and wavelengths simultaneously, the
following vectors are defined:

\[
\phi_j = \begin{bmatrix}
c_{w,1} \left( \frac{k}{s} \right)_{w,\lambda_j} - c_{w,1} \left( \frac{K}{S} \right)_{1,\lambda_j} \\
\vdots \\
c_{w,m} \left( \frac{k}{s} \right)_{w,\lambda_j} - c_{w,m} \left( \frac{K}{S} \right)_{m,\lambda_j}_{m+1}
\end{bmatrix}
\]

Eq. 4.6

\[
\alpha = \begin{bmatrix}
\left( \frac{k}{s} \right)_{\lambda_k} \\
\vdots \\
\left( \frac{k}{s} \right)_{\lambda_k} \\
p_{(k+1)+1}
\end{bmatrix}
\]

Eq. 4.7

\[
\beta_j = \begin{bmatrix}
c_i \left( \frac{K}{S} \right)_{i,\lambda_j} \\
\vdots \\
c_m \left( \frac{K}{S} \right)_{m,\lambda_j}_{m+1}
\end{bmatrix}
\]

Eq. 4.8
\[ Y = \begin{bmatrix} -c_1 \\ \vdots \\ -c_{m+1} \end{bmatrix} \]  

Eq. 4.9

where subscript \( j \) denotes the equation in \( j \)-th wavelength, \( k \) is the total number of wavelengths, \( m \) is the total number of samples in the tint-ladder. The goal is to derive an equation for solving the vector \( \alpha \) containing the relative absorbance coefficient, \((k/s)\) and the impurity index, \( p \). In order to solve the \( \alpha \) for all the tint-ladder and wavelengths, the following sparse matrix and vector are constructed:

\[ \Theta = \begin{bmatrix} Y_j & 0 & 0 & \beta_1 \\ 0 & \ddots & 0 & \vdots \\ 0 & 0 & Y_k & \beta_{k,(m+k)^*} \end{bmatrix} \]  

Eq. 4.10

\[ \Phi = \begin{bmatrix} \phi_1 \\ \vdots \\ \phi_{k,(m+k)^*+1} \end{bmatrix} \]  

Eq. 4.11

where \( \Theta \) denotes a zero vector with the same size as vector \( Y \). Mathematically, Eq. 4.5 is equivalent to Eq. 4.12 where all binary concentrations and wavelengths are taken into account simultaneously:

\[ \Theta \alpha = \Phi \]  

Eq. 4.12

The vector \( \alpha \) can be obtained by minimizing an error function using the least squares method. An alternative solution is to minimize the RMS of spectral error between estimated and actual curves in \((K/S)\) space:

\[ \arg \min_{\alpha} (\Phi - \bar{\Phi}) \]  

Eq. 4.13

Pseudo inverse (denoted by superscript +) is one of the methods that assures global minimum error between actual and estimated curves:

\[ \alpha = \Theta^+ \Phi \]  

Eq. 4.14
4.3.1.2 Masstone-Tint Method

Validity of Masstone-Tint method (Berns and Mohammadi, 2007) for estimating the $k$ and $s$ coefficients in the 2-cte MK theory was verified in the previous section. Analogues formulation can be derived by solving Eq. 4.5 for single tint and masstone. For masstone $c_w=0$ and $c_i=1$, thus Eq. 4.4 is simplified as follows:

\[
\frac{k}{s} = p \left( \frac{K}{S} \right)_{mt,i,\lambda}
\]

Eq. 4.15

In this equation, subscript $mt$ denotes masstone. $(k/s)_{\lambda}$ can be replaced in Eq. 2.55 written for the chromatic mixture. By following simple algebra, $p$ is calculated by a least squares solution as follows:

\[
p = \left[ c_w \left( \frac{k}{s} \right)_{w,\lambda} - c_w \left( \frac{K}{S} \right)_{t,\lambda} \right] \left[ c_t \left( \frac{K}{S} \right)_{t,\lambda} - c_t \left( \frac{K}{S} \right)_{mt,\lambda} \right]^+
\]

Eq. 4.16

Therefore, the purity index ($p$) is calculated using the spectral data of masstone and tint (subscript $t$) mixtures. $(k/s)_{\lambda}$ of the pigment can be calculated using $p$ and Eq. 4.15.

4.3.2 Experimental

The introduced method was evaluated using the similar database of 28 pigments described in Section 4.1.1.1. The experiments were conducted to compare the estimations of 1-KM, 2-KM and the new method. Where the dark masstones cannot be characterized by 2-KM theory, masstones were omitted from the datasets.

4.3.3 Results and Discussion

Three methods were assessed by comparing RMS errors of $K/S$, spectral reflectance and concentration estimations as shown in Figure 4.31 and Figure 4.32. The 2-KM theory produced reasonable spectral estimations compared to the new method and 1-KM theory. Among different pigments, phthalo blue, phthalo green and carbon black produced the largest spectral RMS errors, even when the 2-KM theory was used. This is due to the deviation of KM theory for extremely dark masstones. Other pigments, such as hansa yellow, red oxide and pyrrole red, resulted in poor spectral
approximations for 1-KM and the new method compared to 2-KM. These pigments have scattering properties that cannot be modeled with a portion of the white pigment. In such instances, both $k$ and $s$ coefficients are required for an accurate spectral characterization. In other words, of the three methods, only 2-KM is capable of characterizing the spectral shape the best despite the large estimation errors for extremely dark masstones. Clearly, the improvement does not enhance the spectral estimations effectively compared to 1-KM, since both methods use a single basis function for $(K/S)$ spectral estimations for each pigment.

The mean RMS errors of concentration estimations are shown in Figure 4.32. Looking at the figure, the 2-KM generated the most accurate concentration estimations; 1-KM led to relatively large errors in predictions, particularly for type III pigments, such as diarylide yellow, hansa yellow and yellow ochre. Conversely, concentrations of type II pigments, such as cobalt blue and ultramarine blue, were estimated more accurately. The new modification improved 1-KM for concentration predictions so that the estimated are comparable to 2-KM. The improvement implies the importance of the scattering influence of type III pigments in concentration estimations. Even though a noticeable improvement in spectral matching is not obtained, the new method rectified the concentration estimations remarkably.
Figure 4.31: RMS error of estimating (K/S) values by different methods for 28 pigments. The bars and dots are the mean and median of RMS errors. The pigments are rank ordered based on their opacity index mentioned in pigment specification spreadsheets.
Figure 4.32: Mean RMS error of estimating concentrations by different methods for 28 pigments. The bars and dots are mean and median of RMS errors. The pigments are ordered based on their *opacity index* mentioned in pigment specification spreadsheets.

Total spectral and concentration RMS values for all of the pigments are summarized in Table 4.3. Considering mean and maximum reflectance RMS errors, the 2-KM theory resulted in the smallest RMS errors. The new method led to slightly better spectral estimations than 1-KM. However, concentration estimations were poor using 1-KM.

CIEDE2000 was also calculated as a metric of visual difference between actual and estimated spectra. The mean values of color difference for the 1-KM model and the new method in spectral estimations are ~1.0. However, color difference values for 2-KM are much smaller (~0.2 CIEDE2000) compared to other methods. The mean of concentration estimation improved to ~0.0069 with the new method, compared to ~0.0459 by the 1-KM theory. The mean of concentration estimation for the 2-KM theory is 0.0062, which is close to the results from the new method.
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Table 4.3: CIEDE2000 and total RMS values of spectral reflectance, K/S and concentration estimations.

<table>
<thead>
<tr>
<th></th>
<th>K/S</th>
<th>Reflectance</th>
<th>DE</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.0056</td>
<td>0.0392</td>
<td>0.0391</td>
<td>0.0020</td>
</tr>
<tr>
<td>Variance</td>
<td>0.0001</td>
<td>0.0031</td>
<td>0.0033</td>
<td>0.0000</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.0565</td>
<td>0.3172</td>
<td>0.3365</td>
<td>0.0116</td>
</tr>
<tr>
<td>90th</td>
<td>0.0141</td>
<td>0.1169</td>
<td>0.1058</td>
<td>0.0048</td>
</tr>
</tbody>
</table>

The performance of the different methods was evaluated by comparing the spectral curves of three pigments from the database. The spectral reflectance and K/S curves of the pigments are shown in Figure 4.33. One of the pigments (yellow ochre) is a type III pigment, while the others (ultramarine blue and pyrrole red) are type II pigments. The scattering coefficient of the pigments can also be examined visually by looking at the masstones of each of the pigments. In particular, type II pigments become transparent and dark in their masstone forms; whereas, masstones of type III pigments are rather opaque. Comparing three pigments, ultramarine blue and ochre yellow have a scalable set of K/S curves, as opposed to the pyrrole red pigment. This unscalability of the red pigment affects the spectral estimations of the ramp using the 1-KM theory as expected (see Figure 4.31). On the other hand, 1-KM spectral estimations for ultramarine blue and yellow ochre are close to 2-KM estimations, despite the poor concentration estimations of 1-KM theory. Ochre yellow and ultramarine blue have scalable (K/S) curves; thus, 1-KM theory provides a rather accurate estimation of the ramp using a single basis function for characterizing the pigment properties. The pyrrole pigment ramp, on the other hand, is not perfectly scalable. The K/S RMS errors shown in Figure 4.31 also illustrate larger values for pyrrole red compared to ochre yellow and ultramarine blue pigments.
The ultramarine blue pigment is a perfect case of 1-KM being applied successfully because the scattering of the pigment is negligible (Figure 4.34) and the K/S curves of the ramp are scalable (Figure 4.33). As a result, the RMS errors of spectral and concentration estimations of this pigment are similar for 1-KM and 2-KM. Accordingly, the new proposed method led to the acceptable estimations for spectral and concentration predictions for ultramarine blue. Considering estimated coefficients in Figure 4.34, the impurity index is close to zero, indicating a small amount of scattering for this pigment.
Figure 4.34: Optical coefficients of three pigments derived by each method.
Even though the scalable spectral shape of ochre yellow can be predicted reasonably by the 1-KM theory, the scattering of this pigment is not negligible (see Figure 4.34); thus, the promised assumption for 1-KM is not met. However, this mismatch affects the concentration estimation for this pigment, as shown in Figure 4.32. The plot of actual and estimated concentrations is shown in Figure 4.35. The concentration estimation of the 1-KM theory deviates from the actual values as the scattering of the pigment increases. The concentration estimation error was improved using the modified 1-KM. According to Figure 4.34, estimated unit $k$ of the modified method has a good correlation with the one from 2-KM. This correlation enables optimizing the optical coefficients in two separated steps in PI workflows where pigment coefficients are extracted from a set of random mixtures and a large number of primaries.

The predicted spectral reflectances of the ramps are shown in Figure 4.36, Figure 4.37 and Figure 4.38. The 2-KM method performed well in predicting the spectral reflectances including ramps; the 1-KM and the new method yielded similar spectral estimations for the ramps. Both of the methods generated better spectral estimations for ultramarine blue and yellow ochre, as already explained. The 1-KM and the new method could not characterize the red pyrrole pigment spectral shape as accurately as the other two pigments. However, the 2-KM theory performed well in predicting the spectral curves and concentrations of the ramps for all three pigments.
Figure 4.35: Actual and effective concentrations estimated by different methods.
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Figure 4.36: Actual and estimated K/S and spectral curves by different methods for the ultramarine blue ramp.

Figure 4.37: Actual and estimated K/S and spectral curves by different methods for the yellow ochre ramp.
4.3.4 The Pigment Identification Application

Considering the proposed modification, the 2-KM theory can be simplified into a linear form without the assumption of zero scattering of pigments. This implementation can be seen as an expansion of the 1-KM theory for wider ranges of concentrations and pigments with larger scattering coefficients. The 1-KM concentration estimation can be corrected if the total amount of pigment scattering \((p)\) is known. According to the results, regular linear unmixing algorithms can be used for unmixing purposes. However, since full convexity is not provided, further modifications of linear unmixing methods are required to interrelate the pigment concentrations to the model coefficients. The performance of the modified KM theory for the combinations of pigments is evaluated in the next section.

Estimated unit \(k\) using modified KM method let to similar results from 2-KM. In other words, calculated unit \(k\) from the modified KM method can be a direct estimation for absorption coefficient in 2-KM theory. The scattering coefficients can be derived using 2-KM with known unit \(k\) values. This enables optimizing the
coefficients in two separated steps in PI workflows: 1) extracting unit k according to
light and desaturated pixels, 2) estimating s coefficients using dark and saturated
pixels and estimated unit k. This method reduce the number of unknown variable
that leads to a more stable equation systems.

4.4 Verification of Modified 1-KM for PI

The modified 1-KM model provides a linear relation of K/S of a mixture and the unit
(k/s) curves; yet, the interrelation of the K/S primaries and basis function of a
dimensionality reduction algorithm needs to be determined before using any
unmixing algorithms for PI purposes. Dimensionality reduction is an initial step in
most of the unmixing algorithms to transform a high-dimensional spectral space
into a lower-dimensional space. In the remote sensing field, the spectral vector of a
given pixel is defined as a linear combination of a few endmembers based on a
linear mixing model (LMM). Similarly, for subtractive mixing cases, the spectral
information is reduced to concentrations of the primary pigments with fewer
dimensions. This is important to establish a relationship between primary vectors of
the subtractive mixing model and the results from a dimension reduction method
such as principal component analysis (PCA) or minimum noise fraction (MNF). The
estimated concentrations will be used for 2-KM coefficient estimation in the PI
Chapter due to accurate estimations of the modified 1-KM model. The relationship
between a dimensional-reduction technique (such as PCA) and the subtractive
mixing model is evaluated in this section.

4.4.1 Theory

To establish a link between the modified 1-KM and a dimensional reduction
technique, the modified 1-KM formulation was reformed. Considering Eq. 4.3, the
coefficients of the white component can be expressed as a function of the other
pigment coefficients:

\[
\left( \frac{c_w}{c_w + \Sigma_{i=1}^n (p_i c_i)} \right) = 1 - \left( \frac{\Sigma_{i=1}^n (p_i c_i)}{c_w + \Sigma_{i=1}^n (p_i c_i)} \right)
\]

Eq. 4.17
Combining Eq. 4.17 and Eq. 4.3, the following equation can be derived:

\[
\left( \frac{K}{S} \right)_{mix} = \left( \frac{k}{s} \right)_{w} - \left( \frac{\sum_{i=1}^{n} (p_i c_i)}{c_w + \sum_{i=1}^{n} (p_i c_i)} \right) \left( \frac{k}{s} \right)_{w} + \sum_{i=1}^{n} \left( \frac{c_i}{c_w + \sum_{i=1}^{n} (p_i c_i)} \right) \left( \frac{k_i}{s_w} \right)
\]  

Eq. 4.18

This is equivalent to:

\[
\left( \frac{K}{S} \right)_{mix} - \left( \frac{k}{s} \right)_{w} = \sum_{i=1}^{n} \left[ \left( \frac{k_i}{s_{w}} \right) - p_i \left( \frac{k}{s} \right)_{w} \right] \left( \frac{c_i}{c_w + \sum_{i=1}^{n} (p_i c_i)} \right)
\]  

Eq. 4.19

such that \( \sum_{i=1}^{n} c_i + c_w = 1 \).

This is a key equation implying linearity in the subtractive mixing space. In other words, the K/S values of a given mixture are described as the linear combinations of primary pigments regardless of the impurity index, \( p_i \), of each pigment. Although the impurity index affects the concentration values, the spectral shape of the primary pigments of the primary vectors remain unchanged. The impurity index can be considered as an offset removal for the pigments with higher scattering properties. The spectral shape and concentration values of primary pigments with different impurity indices are convertible mathematically. Considering Eq. 4.19, the white subtracted K/S relates to pigment primaries when the scattering component is subtracted. A convenient way of interpreting this equation is to assume that the primary pigments have impurity values of zero:

\[
\left( \frac{K}{S} \right)_{mix} - \left( \frac{k}{s} \right)_{w} = \sum_{i=1}^{n} \left( \frac{k_i}{s_{w}} \right)_{p} \left( \frac{c_{i,p}}{c_{w,p}} \right)
\]  

Eq. 4.20

where subscript \( p \) denotes pure element with zero impurity index. For any arbitrary impurity index, the corresponding primaries and concentrations can be calculated as follows:

The primaries of any primary pigment, \( (k_i/s_w) \), can be written as its pure primary, \( (k_i/s_w)_{p} \) and the white components, \( (k/s)_{w} \):
\[
\frac{k_i}{S_w} = \frac{k_i}{S_w}_p + p_i \left( \frac{k_i}{S_w}_p \right)
\]

Eq. 4.21

For a given concentration but dissimilar impurity indices, \(p'\), the equivalent primary coefficients can be calculated as follows:

\[
\frac{c_j}{c_w + \sum_{i=1}^{n}(p_i c_i)} = \frac{c'_j}{c'_w + \sum_{i=1}^{n}(p'_i c'_i)}
\]

Eq. 4.22

or

\[
\frac{c_j}{1 + \sum_{i=1}^{n}(p_i - 1)c_i} = \frac{c'_j}{1 + \sum_{i=1}^{n}(p'_i - 1)c'_i}
\]

Eq. 4.23

where \(j\) indicates \(j\)-th primary. Consequently new concentrations can be calculated using the equation below:

\[
c'_j = \left( \frac{c_j}{1 + \sum_{i=1}^{n}(p_i - 1)c_i} \right) + \left( \frac{c_j}{1 + \sum_{i=1}^{n}(p'_i - 1)c'_i} \right) \left( \sum_{i=1}^{n}(p'_i - 1)c'_i \right)
\]

Eq. 4.24

or

\[
(1 - \left( \frac{c_j}{1 + \sum_{i=1}^{n}(p'_i - 1)c'_i} \right))(p'_j - 1) = \left( \frac{c_j}{1 + \sum_{i=1}^{n}(p'_i - 1)c'_i} \right) \left( \sum_{i=1}^{n}(p'_i - 1)c'_i \right) = \left( \frac{c_j}{1 + \sum_{i=1}^{n}(p_i - 1)c_i} \right)
\]

Eq. 4.25

The new concentrations, \(c'\), are calculated by solving a system of equations for all of the concentrations:

\[
\varphi = \begin{bmatrix}
1 - \left( \frac{c_1}{1 + \sum_{i=1}^{n}(p'_i - 1)c_i} \right) (p'_1 - 1) & \ldots & 1 - \left( \frac{c_1}{1 + \sum_{i=1}^{n}(p'_n - 1)c_i} \right) (p'_n - 1)
\vdots & \ddots & \vdots
1 - \left( \frac{c_n}{1 + \sum_{i=1}^{n}(p'_1 - 1)c'_i} \right) (p'_1 - 1) & \ldots & 1 - \left( \frac{c_n}{1 + \sum_{i=1}^{n}(p'_n - 1)c'_i} \right) (p'_n - 1)
\end{bmatrix}_{n \times n}
\]

Eq. 4.26
Defining the following vectors:

\[ C = \begin{bmatrix} c_1' \\ \vdots \\ c_n' \end{bmatrix}_{n \times 1} \tag{Eq. 4.27} \]

\[ \beta = \begin{bmatrix} \frac{c_1}{1 + \sum_{i=1}^{n} (p_i - 1)c_i} \\ \vdots \\ \frac{c_n}{1 + \sum_{i=1}^{n} (p_i - 1)c_i} \end{bmatrix}_{n \times 1} \tag{Eq. 4.28} \]

new concentrations can be calculated using the following equation (superscript -1 denote the inverse matrix):

\[ C' = \varphi^{-1} \beta \tag{Eq. 4.29} \]

### 4.5 Dimensionality Reduction

Principal component analysis and MNF are two popular methods for dimensionality reduction of hyper-spectral data. Analogous to PCA, the MNF (or NAPCA) algorithm decomposes the spectral data to a set of primaries after a noise-whitening step. The eigenvectors of MNF maximize the total SNR instead of the total variation of the spectral image. The rest of the calculations and explanations are similar to regular PCA or SVD.

One difficulty of using KM formulation is to interpret the inherent noise. Unfortunately, the common assumption of additive and independent noise is not valid for the spectral images of this research. The noise is not independent for each wavelength as a result of spectral reconstruction explained in Chapter 3. The spectral values corresponding to each wavelength are reconstructed using a linear combination of camera signals that affect the independency of the noise. On the
other hand, the non-linear transformation to K/S space convolutes the noise interactions. Clearly, the noise does not meet additivity and independency assumptions after transforming the spectral data into the subtractive space. The additivity and independency are the basic pre-requirements for MNF-based dimension reduction algorithms; consequently, MNF-based algorithms cannot be used effectively in the original form of the proposed subtractive mixing space.

The influence of noise can be evaluated by looking at the covariance matrix of a flat-field image after spectral reconstruction, Saunderson correction and transformation into K/S space, which is shown in Figure 4.39 for spectral reflectance and the (K/S) space. The maximum noise variance for spectral reflectance and (K/S) images are \(~8\times10^{-5}\) and \(~1\times10^{-6}\) respectively, which are fairly small values. The noise variance is not independent for each band, as already explained. Additionally, the noise values are larger for longer wavelengths. The covariance matrix of the dark current image (Figure 4.40) also implies the dependency of the noise on the intensity of the signal, which makes the noise analysis more complicated. Despite the complexity of noise, its contribution can be reduced in the measurement step by controlling the acquisition condition and averaging more images to gain larger SNR. As shown in Figure 4.39 and Figure 4.40, the noise fraction of \(~10^5\) is large enough to neglect the noise. Finally, the regular PCA was chosen for dimension reduction for further analyses.
Figure 4.39: Covariance of the flat field image in spectral reflectance (top) and (K/S) (bottom) domains.

Figure 4.40: Covariance of the dark current image in spectral reflectance space.
It should be noted that PCA has been suggested and examined for pigment identifications but in spectral reflectance space as explained in Section 2.6. However, spectral reflectance space does not interrelate the pigment concentration and mixtures spectral behavior linearly. Consequently, the primary pigments cannot be extracted using regular spectral unmixing algorithms defined in remote sensing. An example of PCA coefficients in K/S and reflectance spaces for a test painting, shown Figure 4.41, clarified that reflectance space did not provide a linear relationship between the PCA and pigment concentrations.

Figure 4.41: PCA coefficients of a spectral data from a painting 2-3-2 (c) comprised of three primary pigments in reflectance (b) and K/S (a) spaces. The black dot represents the white component. For more information about the painting see Appendix E.

The next step is to derive a link between 1-KM and PCA coefficients. Considering Eq. 4.20, it corresponds to the PCA definitions in which white-subtracted K/S vectors are decomposed into the primary K/S vectors. Similarly, any \((K/S)_c\) curve of the image can be expressed as a linear combination of a set of eigenvectors applying PCA:

\[
\begin{bmatrix}
\frac{K}{S}_c \\
\end{bmatrix} = \begin{bmatrix}
\frac{K}{S}_{mix} \\
\end{bmatrix} - \begin{bmatrix}
\overline{\frac{K}{S}} \\
\end{bmatrix} = UP 
\]

where \(\begin{bmatrix}
\frac{K}{S}_c \\
\end{bmatrix}\) is K/S curve after mean subtraction. \(U\) is the matrix of the most significant eigenvectors calculated from the covariance matrix of \(\begin{bmatrix}
\frac{K}{S}_{mix} \\
\end{bmatrix}\). Combining Eq. 4.20 and Eq. 4.30 for pure primaries equation below is obtained:

\[
UP + \overline{\begin{bmatrix}
\frac{K}{S} \\
\end{bmatrix}} = \begin{bmatrix}
\frac{K}{S} \\
\end{bmatrix}_p C + \begin{bmatrix}
\frac{K}{S} \\
\end{bmatrix}_w \]

Eq. 4.31
The corresponding coordinate of the subtractive primaries \( \left( \frac{K}{S} \right)_p \) can be calculated as follows:

\[
U_P + \left( \frac{K}{S} \right) - \left( \frac{k}{S} \right)_w = \left( \frac{K}{S} \right)_p \mathbf{C}
\]  
Eq. 4.32

Setting \( \left( \frac{k}{S} \right)_{w,c} = \left( \frac{k}{S} \right) - \left( \frac{k}{S} \right)_w : \)

\[
U_P - \left( \frac{k}{S} \right)_{w,c} = \left( \frac{K}{S} \right)_p \mathbf{C}
\]  
Eq. 4.33

and \( P_w = U \left( \frac{k}{S} \right) \), following equation is derived:

\[
U(P - P_w) = \left( \frac{K}{S} \right)_p \mathbf{C}
\]  
Eq. 4.34

According to this equation, \( P = (P - P_w) \) can be represented as a vector in the PCA space that specifies the PCA coefficients from the origin when the origin corresponds to the white component. As a result, Eq. 4.34 is simplified as follows:

\[
U_P = \left( \frac{K}{S} \right)_p \mathbf{C}
\]  
Eq. 4.35

For primary pigments the concentration matrix is the identity matrix. The primaries can be calculated according to the corresponding eigenvectors and centralized coefficients, \( P_{pr} \), as follows:

\[
\left( \frac{K}{S} \right)_p = U_{P_{pr}}
\]  
Eq. 4.36

Vector \( P_{pr} \) are extracted using unmixing algorithms in the reduced space. The actual concentration matrix, \( \mathbf{C} \), is calculated as follows:

\[
\mathbf{C} = \left( \frac{K}{S} \right)_p^+ U_P = (P_{pr})^+ P
\]  
Eq. 4.37
Eq. 4.37 can be interpreted as the projection of the $P$ into the primary vectors $P_{pr}$. Both $(\frac{K}{S})_{mix} - (\frac{K}{S})_{M}$ and $(\frac{K}{S})_{mix} - (\frac{K}{S})_w$ span the same space if 1-KM is perfectly valid. In addition, the dimensionality of the subtractive mixing space will be the number of significant eigenvalues of PCA. In fact, the significant eigenvectors, $U$, are a rotation form of the pure primary vectors $(k/s)_p$:

$$U = \left(\frac{K}{S}\right)_p M$$  \hspace{1cm} \text{Eq. 4.38}

It is important to mention that the length of the vectors of $(\frac{K}{S})_p$ is not a crucial factor since it will be normalized by the rotation matrix, $M$. Accordingly, the primary vectors with the maximum magnitude are not optimum choices for pure element selection because the subtractive linear model yields better linearity for lighter shades. Binary mixtures of pure elements and white are scaled forms of the unit $(\frac{K}{S})_p$ in subtractive space and can be used for calculating $(\frac{K}{S})_p$.

According to Eq. 4.38, 1-KM and PCA primaries are interrelated by a rotation matrix. It means that PCA can also be used for evaluating the performance of 1-KM. The performances of KM and 1-KM theories were previously evaluated in Chapter 4. Here, the performance of the model is assessed with three chromatic pigments in the mixtures to determine a region where the linear subtractive mixing model is valid. The pigment identification algorithm is applied within the ranges where the 1-KM theory maintains this validity. According to the interrelation of 1-KM and PCA eigenvectors, the performance of the 1-KM can be evaluated by analyzing PCA eigenvalues and eigenvectors.

### 4.6 Experimental

Experiments are based on different combinations of three chromatic pigments, used Section 4.1.1.1. The $(K/S)$ curves of the mixtures were estimated by the unit $(k/s)$ values of the primary pigments and 1-KM theory. The unit $(k/s)$ values of each one
of the pigments were obtained using a non-negative linear least-squares method and by minimizing the RMS error of actual and estimated (K/S) values. The goal was to evaluate the performance of the 1-KM theory for spectral reconstruction of the mixtures associated with the training datasets. The testing and training datasets used in this section are shown in Table 4.4 and Table 4.5. Even though the masststones cannot be characterized by 2-KM theory accurately, they were included in both the validation and training datasets for a general evaluation.

The spectral reflectances and CIELAB values were extracted as explained in Section 4.1.1.2. The pale dataset consisted of the 61 samples with CIELAB L* greater than 50 and CIELAB C* smaller than 50, selected from the database. This selection of the mixtures is based on the results from the previous section and by removing high-scattering mixtures.

<table>
<thead>
<tr>
<th>Table 4.4: Testing Datasets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Testing Datasets</td>
</tr>
<tr>
<td>Tint Ladders and Masstones</td>
</tr>
<tr>
<td>All Mixtures</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.5: Training Datasets for PCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Testing Datasets</td>
</tr>
<tr>
<td>Tint Ladders and Masstones</td>
</tr>
<tr>
<td>Tint Ladders No Masstones</td>
</tr>
<tr>
<td>All Mixtures No Masstones</td>
</tr>
<tr>
<td>All Mixtures</td>
</tr>
<tr>
<td>Pale Tints</td>
</tr>
</tbody>
</table>

### 4.7 Results and Discussions

The result of the K/S estimations for the pigment ramps when tint ladders and masststones were used as a training set are shown in Figure 4.42. The unit (k/s) coefficients are derived for three pigments simultaneously as opposed to independent evaluations for each pigment. Since the spectral ramp is not scalable,
the optimized \((k/s)\) coefficients do not produce proper predictions particularly for higher concentrations and type II pigments, resulting from the unscalability of the ramps. The reflectance RMS errors, as well as CIELAB difference, implied poor perceptual predictions. The estimated \((k/s)\) coefficients led to unacceptable estimations for the rest of the pigment combinations as shown in Figure 4.43.
Figure 4.42: The result of K/S estimations for the three pigment ramps when tint ladders and masstones are used as the training set. Actual (dotted lines) and predicted (solid lines) spectral curves in K/S (b) and spectral reflectance (a) spaces. (c) CIELAB L*-C* plot of actual (filled circles) and (lines) predicted samples of the ramps of three pigments.
Figure 4.43: CIELAB L*-C* plots of actual (filled circles) and predicted (lines) of all the mixtures (126 samples) when tint ladders and masstones are used as training set.

The performance of predictions improved when the pigment spectral curves are scalable in (K/S) space. This scalability coincides with highly scattering mixtures as the required assumption for the 1-KM theory. The spectral estimations in K/S and the reflectance space are shown in Figure 4.44. Here, the training data are narrowed to the first five light mixtures. The estimation results for all 126 mixtures led to a considerable improvement for light and mid-shade mixture predictions (Figure 4.45). The RMS errors for masstones and dark mixtures, increased; however, the estimation error is still comparable to the previous dataset. It must be noted that the improper KM coefficients might lead to negative predictions, which increase the RMS errors for dark mixtures.
Figure 4.44: The result of K/S estimations for the three pigment ramps when light patches of light patches of the ladders are used as the training set. Actual (dotted lines) and predicted (solid lines) spectral curves in K/S (b) and spectral reflectance (a) spaces. (c) CIELAB L*-C* plot of actual (filled circles) and (lines) predicted samples of the ramps of three pigments.
The use of piecewise training sets for dark and light was also examined for better evaluations. This method already was discussed in Section 4.1.2.2.4 but for the 2-KM theory. The predictions confirmed the results that calculated coefficients do not improve the estimations even for dark mixtures and the masstones. Meanwhile, the risk of large errors increased noticeability for light- and mid-shade mixtures.

In summary, the 1-KM theory, as a linear subtractive mixing model, was valid for light mixtures with scalable curves in K/S space. This functional region for the 1-KM theory depends on the scattering, absorption and strength of the pigment under examination. This region can be specified in the CIELAB color space for most of the pigments evaluated. For example, the mixtures with $L^*$ greater than $\sim$50 and $C_{ab}^*$ smaller than $\sim$50 led to acceptable predictions using 1-KM. The concentration estimations were rather precise even for dark mixtures, as explained in Section 4.1.2.2.3. Accurate concentration predictions for saturated and dark mixtures is a
noticeable outcome that can be utilized for estimating the 2-KM optical coefficients in the pigment identification pipeline.

4.8 Conclusions

The performance of KM for developing a linear mixing model was studied in this chapter. The general applicability of the 2-KM and 1-KM theories was examined for pigment identification. A modification of 1-KM was introduced to extend the valid concentration range and improved the concentration estimations for the 1-KM theory. The proposed version of 1-KM maintained its linearity enabling the use of linear mixing model for pigment identifications. Finally, the relationship of the concentrations of the modified 1-KM and the coefficients of a dimensionality reduction method were derived mathematically.

The applicability of the KM theory was examined for different training data with a wide concentration range. In general, the KM theory provides an acceptable characterization of subtractive mixtures of binary and combinations of chromatic pigments except for dark mixtures and masststones. The largest errors corresponded to type II pigments with a small amount of scattering coefficient.

The training data should contain both high and low concentrations of the mixtures to have enough modulation for coefficient optimizations. Light masststones (type III pigments) can be used for coefficient estimations where the KM theory maintains it validity. Despite the large errors of dark masststones for training data, training datasets of light mixtures and masststones produced reasonable predictions by covering curve shapes of light and dark mixtures.

The proposed modification of 1-KM theory enhanced the concentration estimations of the paint layers. In the proposed method, the scattering of the chromatic pigments was set to a portion of the scattering of the white pigment. The scattering property of the pigments was described by a scalar called the impurity index. This
assumption improved 1-KM concentration estimations while keeping the linearity in the \((K/S)\) spectral space.

Finally, the applicability of the modified 1-KM theory for pigment identifications was studied. The 1-KM theory and PCA formulations were analyzed and a proper set of equation was derived for interrelating pigment concentrations and PCA coefficients. Since the linearity of the subtractive mixing model is vital for pigment identification, a reliable region in which 1-KM is valid was indicated. Masstones, dark mixtures and extremely saturated mixtures usually deviated from the linearity of the KM theory and are not recommended for pigment identifications.
CHAPTER 5: KM-BASED PIGMENT IDENTIFICATION FOR PAINTINGS

The basics of image-based pigment identification (PI) are quite similar to spectral unmixing techniques, but in a subtractive mixing space. As already explained in Section 2.7.3, most of the available unmixing algorithms have been developed and evaluated based on a linear mixing model (LMM). Theoretically, similar algorithms can be used for PI when a linear subtractive mixing model is available. A KM-based linear mixing model was already introduced and evaluated in Chapter 4. According to Eq. 4.3 and Eq. 4.19, paint mixtures can be expressed as a linear combination of the primary pigments; however, the fractions of the primaries are specified by a ratio of actual concentrations, rather than the concentrations themselves. The concentration ratios can be more than unity and, therefore, the summation to unity and convexity assumptions are violated. This deviation from full convexity requires further modifications of common unmixing algorithms for PI, which is discussed in this Chapter. A demonstration of differences between actual concentrations against a ratio of concentrations can be observed in Figure 5.1. In this figure, the initial proportions have a uniform distribution however the concentration ratio follows a different distribution function. Additionally, the coefficients of the pure elements are large and not quite predictable.
KM-BASED PIGMENT IDENTIFICATION FOR PAINTINGS

5.1 Unmixing Algorithms

Unmixing algorithms were studied for a variety of aspects, including speed, efficiency, simplicity and more importantly, eligibility for further modifications according to subtractive mixing characteristics. For instance, most of the conical-based unmixing algorithms could not be instantly applied to the data because of its convexity violation. Other examples include geometric and simplex-based methods that could not be utilized directly for unmixing purposes for a similar reason. However, most of the geometric based unmixing algorithms were capable of being modified to fit into the modified 1-KM model for pigment identification.

The pigment identification pipeline was designed depicted in to Figure 5.2. The process starts with the spectral image after surface correction as discussed in Chapter 3. In the exemplar selection step, the spectral image is processed in terms of the size and preliminary segmentations to obtain significant information for the unmixing algorithm. This process involves removing unnecessary or redundant pixels for dimensionality reduction. The selected set of data points is converted into the K/S space for dimensional reduction and unmixing. Thereafter, a Pixel Purity Index (PPI) technique is applied to the data to extract the boundary pixels after dimensionality reduction. Then, a simplex-growing-unmixing algorithm (SGA)

Figure 5.1: Simulated distribution of the mixture coefficients in additive and subtractive mixing models. (a) is the actual concentrations of the primaries, (b) is the ratio of concentrations.
extracts independent signatures from the exemplar pixels. The endmember extraction procedure is followed by a sparsity-promoting-iterative-endmember detection (SPICE) method for refining the basis functions obtained from the SGA. This step is necessary in cases where no pure pixels are in the image. The SPICE algorithm is based on a non-linear and iterative optimization that minimizes an objective function to yield a tight fit to the dataset. Both SGA and SPICE algorithms must be modified to fit in the subtractive mixing model. Predicted endmembers are compared to an available pigment database in order to select a set of actual pigments. Eventually, The concentration map for each pigment can be obtained by projecting the (K/S) value of each pixel onto the primary (K/S) vectors. Each step is explained in more detail in the following sections.

**Figure 5.2:** The pipeline for pigment identification.
5.2 Exemplar Selection

The spectral images from the acquisition system are large and contain a considerable amount of redundant information. The *Exemplar Selection* is a filtration process to obtain a reasonable number of the pixels representing the entire image. It is also necessary to remove dark and saturated pixels as explained in Chapter 4.

Dark and saturated pixels are omitted with respect to their spectral reflectance, CIELAB $L^*$ and CIE $C_{ab}^*$ values. According to previous results, a secure region for a subtractive mixing prediction is about CIELAB $L^*$ of [50-100] and $C_{ab}^*$ of [0-50]. The small, negative or spectral values greater than unity are omitted by restricting spectra between certain numbers (usually [0.1-1]). It should be mentioned that the spectral values can be negative or greater than unity as a result of spectral characterization and measurement noise. The measured spectral reflectance longer wavelengths usually contains lower SNR values that lead to noisy spectral acquisitions. An example of exemplar selection is shown in Figure 5.3.

![Original Image](image1.png) ![Processed Image](image2.png)

**Figure 5.3:** The first step of Exemplar Selection procedure maintaining $L^*$ of [50-100] and $C^*$ of [0-50].
All the pixels from captured images of the LCTF capturing system, with 1.2-Megapixel resolution, cannot be analyzed in practice due to the large number of pixels. A simple downsampling method is an alternative to reduce the number of pixels to typically several thousands. It is important not to use any interpolation- or smoothing-based techniques in the spectral space since they cause unwanted variations in the subtractive space. A recommended down-sampling method is the nearest neighbor method in which the closest pixels are picked with no further manipulations.

The distribution of representative pixels also affects dimensionality reduction and unmixing steps. In a uniform downsampling method, the probability of the selecting pixels corresponds to their abundances. The exemplar selection methods are useful to achieve a better distribution of spectral curves and eliminate unwanted redundancies. One possible alternative is selecting the pixels with the maximum distance according to a distance function. The algorithm starts by choosing the first exemplar pixel, which can be the lightest pixel in the image. Next, the pixel with the maximum distance to previously selected pixels is picked from the image. The successive process of pixel selection continues until the desired numbers of pixels are extracted. Either spectral reflectance or K/S space distance functions, such as angular-based or RMS-based distance functions, can be utilized for spectral distance calculations. Spectral comparisons in the spectral reflectance space result in light colors since they have larger distances in this space. On the other hand, the K/S-based distance function yields darker colors with larger K/S quantities. In most cases, a spectral reflectance-based distance function led to stable results compared to the K/S-based one. An example of the pixel selection of an examined spectral image is shown in Figure 5.4. Note that comparing all the image pixels to the previously selected pixels is computationally expensive; therefore, the pixel selection was performed for rows and columns of the image independently, then a global pixel selection was applied to the subsampled data.
Figure 5.4: 1000 exemplar pixels from the original image according to the spectral curves of the images.

The down-sampled set of pixels mostly contains blue and dark colors according to the image content. The maximum reflectance distance method yields a uniform distribution of spectral values, with less sensitivity to the image content. Similarly, maximum K/S distance led to the selection of dark and saturated pixels with a uniform distribution in K/S space.

In practice, the exemplar selection algorithm was applied to the pixels within the predefined ranges of CIELAB L* and CIELAB C*. Differences in the exemplar selection are demonstrated at Figure 5.5 and Figure 5.4. Notice that the selected
pixels in spectral and K/S-based distance methods are rather uniform, even though the number of orange and yellow pixels is relatively small in the filtered image.

![Filtered Image](image)

Figure 5.5: 1000 exemplar pixels from the original image after removing dark and saturated points.

The drawback of extracting a uniformly distributed sub-set of spectral pixels is its sensitivity to noisy data. Any pixels with uncharacterized spectral shape will be maintained as exemplar pixels. Acquisition noise level, spatial resolution, optical aberrations, etc. lead to unreal spectral shapes and intensify the problem. Improving measurement precision and resolution are possible solutions to this problem; other post-processing methods, such as image edge removal and clustering techniques are alternative remedies.
Figure 5.6 is an illustration of false spectral curves within a spectral image. In this figure, specified yellowish pixels are the result of inaccurate spectral measurement. There is no yellow pigment used in this painting, as shown in the high-resolution image. The spectral values of the edges are blurred dissimilarly for each spectral channel, which produced incorrect spectral reflectances. Optical blurring, defocusing, optical geometric aberration and spatial resolution of the camera are other examples that cause failures in spectral imagery.

Figure 5.6: An example of the images containing pixels with false spectral shapes. Images in the top row are rendered from the low spatial resolution spectral image; images at the bottom are obtained from a high-resolution trichromatic camera.

Removing the high frequency content is an alternative to avoid selecting uncharacterized pixels. The high-frequency areas can be identified and omitted by a simple edge detection algorithm. The result of removing high frequency pixels is
illustrated in Figure 5.7. The algorithm removes high-frequency regions within a 5x5 pixel Gaussian kernel and a threshold. The kernel size and the threshold value are selected manually based on the optical priorities of the acquisition system.

---

![zoomed area](image)

**Figure 5.7:** A rendering of the spectral image after excluding the pixels corresponding to the edges.

### 5.3 Dimensionality Reduction

Principal component analysis (PCA) was selected for dimensionality reduction of the spectra in the subtractive mixing space as already discussed in Section 4.5. The most significant eigenvectors of the exemplar data were extracted according to a predefined number of primaries. Projecting the mean-subtracted data to the orthonormal PCA eigenvectors, the PCA coefficients of the data were derived. The unmixing processes are performed to the PCA coefficients for endmember extraction thereafter. Eventually, PCA coefficients of the pure elements are converted back to the high dimensional K/S space in a reverse path.

### 5.4 Pigment Identification Algorithms

Two unmixing algorithms were chosen and modified for pigment identification. The modifications mostly address the convexity issue of the subtractive mixing model and an accurate estimation for the white component. Both of the unmixing
algorithms were applied to the pure pixels from a pixel purity index (PPI)-based algorithm.

### 5.4.1 Pixel Purity Index (PPI)

Pixel purity index (PPI) is one of the common approaches for endmember extraction in the literature. The algorithm is implemented either for the original or the dimensionally reduced spectral data. Commonly, PPI is applied to reduced data to reduce processing time and eliminate the effect of noise. The results, therefore, are considered as an intermediate step for further unmixing algorithms.

The original PPI algorithm was modified to address the convexity issue in the subtractive mixing model. Accordingly, PPI was applied to a subset of data with different lightness values in a series of iterations. The modified PPI algorithm can be described as follows:

\[
C_{L^*,\text{Max}} = \text{Coefficients Corresponded to } L^*_{\text{max}} \\
C_{\text{int}} = \text{Coefficients Corresponded to } L^*_{\text{int}} = L^*_{\text{max}} - L^*_{\text{min}} \\
\text{Loop } L^* = 1 \text{ to } L^*_{\text{int}} \\
\quad C_{L^*} = \text{Coefficients Corresponded to } L^*_{\text{int}} \\
\quad \text{InitialPixels} = \text{Pixels with Coefficients } ||C_{L^*,\text{Max}}|| < ||C|| < ||C_{L^*,\text{Max}} - C_L|| \\
\quad \text{PurePixels} = \text{Call Function ExtractPurePixel(InitialPixels)} \\
\quad \text{TotalPurePixels} = [\text{TotalPurePixels, PurePixels}] \\
\text{End Loop}
\]

An illustration of the modified PPI method is shown in Figure 5.8. Before starting the selection loop, the PCA coefficients were centralized so that the white component had a value of 0 vector; therefore, the length of each point represented the distance to the predefined white. The white component corresponded to an ideal or pre-defined white that is chosen by the user. The choice of white component is not critical in this step since it is only used for distance calculation for filtering the
candidate pixels. The final estimation of the white component is explained in the next steps.

Figure 5.8: An illustration of the implemented PPI algorithm in a plane of two PCA coefficients. In each iteration, the pixels associated with a range of L* are evaluated.

The PPI algorithm was implemented to specify three sets of pure pixels. The first set included the total selection of pure pixels, applicable for iterative endmember extraction algorithms (Section 5.4.3) and maximizing sparsity. The second selection of pure pixels contained pure pixels when light mixtures were omitted, applicable for extracting endmembers using the geometric algorithm (Section 5.4.2). The third selection of pure pixels enclosed light mixtures for estimating the actual white. An example of different sets of pure pixels for a spectral image is shown in Figure 5.9.
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Figure 5.9: 2D demonstration of PCA coefficient for a test image showing the modified PPI algorithm for extracting three sets of pure pixels.

PPI1: Sparse Set

\[ L^*_{\text{max}} = L^*_w \]
\[ L^*_{\text{min}} = L^*_w - 50 \]

PPI2: Primary Selection Set

\[ L^*_{\text{max}} = L^*_w - 15 \]
\[ L^*_{\text{min}} = L^*_w - 50 \]

PPI3: White Selection Set

\[ L^*_{\text{max}} = L^*_w \]
\[ L^*_{\text{min}} = L^*_w - 5 \]
The number of random vectors, or skewers, and the threshold of pure pixels are two parameters that need to be specified manually. The number of skewers is usually set to a large number to make sure a sufficient number of projections is applied to the data. The number of projections can be adjusted as a function of dimensionality of the data. Clearly, more projections are required for larger dimensionalities. For this research, the number of random projections (for each iteration of L*) and pixel purity threshold were set to 1000 and, 3 respectively. The PPI threshold was set to a small number to reduce the chance of losing pure elements in geometric and non-linear optimization steps.

Extracted pure pixels can be the subject of further cluster analyses and pattern recognitions. Data processing methods, such as n-dimensional K-Means and RANSAC, have been investigated for cluster analysis of the pure pixels according to L2 Euclidean and spectral angular mapper (SAM) dissimilarity functions; however, most of the methods ended up with extra and complicated adjustments in practice. The pure pixels passed to the next step directly and without further processing to maintain the simplicity and flexibility of the workflow.

5.4.2 Simplex Growing Algorithm (SGA)

Two geometric-based algorithms were examined based on N-Finder and the simplex growing algorithm (SGA). N-Finder is an automated endmember extraction algorithm that searches the set of pixels of a simplex with maximum volume. The algorithm starts with three initial pixels and continues by adding a randomly selected pixel to attain the maximum volume for the endmembers (for more details of the method see Section 2.7.3.2). The goal is to modify N-Finder to meet the required assumptions of the subtractive mixing model. The volume minimization procedure was replaced by volume minimization of a normalized tetrahedral. It should be remembered that the aim of PI is to extract a mixture of pure elements with the white component; therefore, the extracted endmembers should be selected from the edges of the simplex rather than the corners. The normalization step
removes the dependency of the searching process to the length of the chosen endmembers. Additionally, the volume calculation can be replaced by the formula introduced by Berman, et al. (Berman, et al., 2004) for reducing the processing time. The modified objective function, $RSS^*_{SGA}$, was defined as follows:

$$RSS^*_{SGA} = (1 - \mu) \frac{RSS}{N} + \mu SSD_n$$  \hspace{1cm} \text{Eq. 5.1}$$

$$SSD_n = \sum_{k=1}^{M-1} \sum_{l=2}^{M} \left( \frac{E_k}{\|E_k\|} - \frac{E_l}{\|E_l\|} \right)^2 = M(M-1)V'$$  \hspace{1cm} \text{Eq. 5.2}$$

where $M$ and $N$ are the number of endmembers and of pixels under examination, respectively. $RSS$ is the square sum of the estimation errors similar to the ICE algorithm explained in 2.7.3.7. $V$ is the sum of variances (over the bands) of the normalized endmembers. The term $SSD_n$ is the sum of squared distances of normalized endmembers, which is correlated to the volume of the simplex. $\mu$ is a regularization parameter adjusting the contribution of each term set to 0.01. To improve the speed of the calculation, the random pixels were selected from the second set of pure pixels rather than the entire image. Finally, the pixel set with the minimum $RSS^*_{SGA}$ was chosen as the best endmembers. The selected endmembers were used as initial values to a simulated annealing (SA) algorithm for further refinements.

The SGA implementation is similar to the N-Finder, but the candidate pixels are not selected randomly. The algorithm starts with a single endmember that minimizes the objective function. The next endmember is found through searching the pure pixels, so the new hyper-plane has the smallest $RSS^*_{SGA}$. The SGA is faster and the results are comparable to those of N-Finder (Chang, et al., 2006). Accordingly, the SGA was preferred over the N-Finder technique for pigment identification for this dissertation.
A reasonable estimation of the white component is vital for pigment identification. As a result, the SGA is designed in three steps for an adequate estimation of the white component and endmembers:

1. The estimation of primaries based on a predefined white, followed by SA refinement,
2. The estimation of the white point from the image, and
3. The estimation of the endmembers according to the new white point, followed by SA refinement.

In the first step, the algorithm is executed by using a pre-defined white. The white component can be based on pre-existing information or a reasonable choice of a non-selective white such as titanium dioxide. Further refinements are performed using a SA-based algorithm in which a new set of endmembers with smaller objective function is extracted using a sequential search. In the SA algorithm, new candidates are selected from the neighbor points of the initially selected endmembers.

After extracting the primitive selections of the endmembers, the white component is estimated through a search procedure of candidate pure pixels for white (pure pixels in the third set). The pure pixel with the smallest objective function is marked as the white component. Afterwards, the SGA and SA algorithms are repeated based on the new white component. Finally, the extracted endmembers are rescaled to have the maximum value of unity based on the coordinates of the white component.

An example of the SGA algorithm for a simulated painting with a yellowish white primary is shown in Figure 5.10. The algorithm starts using titanium white as the white component and extracts a set of primitive primaries. Selected primaries are normalized to unit (k/s) values and set the concentration coefficients as unity. The normalization is carried out according to the white point coordinate; therefore, the normalizing process is incorrect (Figure 5.10 a). The correct white point is specified using the extracted actual primaries from the previous step (Figure 5.10 b). Finally,
the SGA is repeated utilizing the new white point (Figure 5.10 c). The SGA notation refers to the SGA together with the SA algorithms for simplicity hereafter.

The extracted primaries from the first and third steps are useful depending on the existence of the white component in the painting. If there is no pure pixel of white component, the results from the first SGA are applicable; otherwise, the other set of primaries must be used. Noted that the white component can also be derived from the optimization step.
Figure 5.10: Three steps of the SGA for pigment identification. The black circle is the position of selection white. The red circles are the selected pixels according to the SGA algorithms and the green circles are the normalized coefficients.
5.4.3 Non-Linear Optimization

Pixel Purity index and SGA indicate pure pixels when pure elements are already present in the painting. In another category of unmixing methods, the pure elements are extracted according to a statistical model in the case of an absence of pure pixels in the image. Two optimization-based unmixing algorithms were chosen for further implementation and evaluation: iterated constrained endmember (ICE) and sparsity promoting iterated constrained endmember (SPICE). In both methods, the endmembers are optimized iteratively subject to an objective function and a set of constraints. Likewise, the objective function should be modified to fit into the subtractive mixture conditions.

The ICE algorithm extracts the endmembers in an iteration that minimizes the RSS. The minimization is subject to positivity, summation to unity for the proportions and the shrinking the volume of the simplex. The ICE algorithm converges to a simplex that fits the dataset. Adding the sparsity term pushes the iteration toward tighter fits to the edges and vertices. The SPICE algorithm is an extended version of ICE that is configured for sparsity. The SPICE algorithm produces better results for sparse set of points, such as those obtained from the PPI algorithm, which meanwhile expedites the calculation speed.

The original form of the iterative-based algorithm was modified for the subtractive mixing model. A new sparsity term was added to the objective function for better estimation of the white component. The modification was based on the knowledge of higher percentage of the white component in the mixtures. This modification also reduced the sensitivity of the optimization to dark pixels, simultaneously. A new sparsity regularization term, $SPT_{w}$, was developed to improve SPICE for subtractive mixtures:

$$SPT_{w} = \sum_{l=1}^{N} \gamma_{k} \sum_{k=2}^{M} |p_{lk}|$$

Eq. 5.3
The final sparsity term is defined as the average of two sparsity terms:

\[ SPT_m = \frac{1}{2} SPT_w + \frac{1}{2} SPT \]  
Eq. 5.4

\( SPT \) is the original sparsity term defined in the SPICE method according to Eq. 2.31 (Zare, and Gader, 2007). \( SPT_w \) is a new sparsity term that assigns more weight to the light colors and the white component. Notice that the second index in the summations, \( k \), starts from 2. Assuming the first component, \( k=1 \), corresponds to the white component, the sparsity term removes the white component for sparsity calculations. The regularization term, \( \mu \), was set to 0.1 as recommended in the literature. The functionality of each sparsity term is demonstrated in Figure 5.11. The performance of the traditional sparsity term is illustrated in Figure 5.11a. Note that the points outside the simplex of the defined primaries tend to increase in the sparsity term. The second sparsity term gains large values when points get further from the white component Figure 5.11b. The final sparsity term is the average of both sparsity terms (Figure 5.11) leading the optimization to converge having a tighter fit for light mixtures.
Figure 5.11: A colormap illustration of different sparsity terms. Pink and the white points are simulated representatives of endmembers and white component, respectively. Blue and red areas show smaller and larger values of the sparsity function.
The selection of initial values for the non-linear optimization influences the final results. In practice, the output of the SGA was used for initiations. Analogous to geometric unmixing, the non-linear optimization can be set for a pre-defined white or optimizing the white component simultaneously along with other endmembers.

Any negative values in estimated endmembers in \((K/S)\) space were avoided by setting the positivity constraint. Positive endmembers are more realistic and convenient for calculating spectral reflectance of the endmembers. Therefore, the white component and the endmembers were optimized subject to the positivity:

\[
\left( \frac{K}{S} \right)_w = U_{Pw} + \left( \frac{K}{S} \right)_w \geq 0
\]  
Eq. 5.5

\[
\left( \frac{K}{S} \right)_p = U_{Pp}, \left( \frac{K}{S} \right)_p \geq 0
\]  
Eq. 5.6

### 5.5 Number of Primary Pigments and Number of Orthogonal Primaries

Intrinsic dimensionality (ID) of the data corresponds to the number of independent primary vectors for describing the high-dimensional data that can differ from the number of primary pigments used for creating the painting. If the constituent primaries are linearly dependent, the ID is smaller than the actual number of primary pigments. Determination of the effective number of pigments is a substantial piece of the pigment identification process, which is discussed in this section.

The majority of the ID determination algorithms analyze the properties of the eigenvalues and noise covariance. The RMT, HySime and Gram Matrix are three ID algorithms that were examined for subtractive mixtures. The RMT and HySime methods evaluate the noise covariance matrix and eigenvalues for ID determination, as explained in Section 2.7.4.3. In practice, these methods overestimated the number of primary elements because of the model deviating away from perfect linearity.
Instead, the Gram Matrix method investigates the dependency of the extracted endmembers using geometrical calculations. For this research, a Gram matrix-based method was developed with less sensitivity to the nonlinearity of the model. The algorithm is comprised of two steps. First, the total number of eigenvectors corresponding to a total variability of $\sim 99.99\%$ is selected. Extra eigenvectors with no significant amount of information should not be selected because of matrix singularity problems in inverse pathways. However, since the eigenvalues correspond to the orthogonal axes, the contribution of non-orthogonal actual pigments might not be evaluated effectively. Next, the SGA extracts the endmembers from the pure pixels associated with the selected dimensionality. The number of initial endmembers starts from three and increases successively. In each step, the relative volume of normalized endmembers is calculated according to Eq. 5.9. The calculated volume is divided to the hyper-tetrahedron with the same number of normalized vertices to remove the effect of dimensionality. If the new endmember does not add any independent information to the previously selected endmembers, the volume of the normalized simplex becomes zero. In contrast, if the new element is orthogonal to the previous hyper-plane, the ratio will be unity. Plotting the $SSD_m$ against the number of extracted endmembers gives an estimation of primary pigments yielded.

$$\Psi = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$  \hspace{1cm} \text{Eq. 5.7}

$$SSD_u = \sum_{k=1}^{M-1} \sum_{l=2}^{M} (\Psi_k - \Psi_l)^2 = M_u (M_u - 1) V_u$$  \hspace{1cm} \text{Eq. 5.8}

$$SSD_m = \frac{SSD_n}{SSD_u}$$  \hspace{1cm} \text{Eq. 5.9}

$SSD_u$ is the metric of the volume of unit hyper-tetrahedron, with orthonormal vertexes. $I$ and $\theta$ are identity matrix and zero vector, respectively, which define the unit hyper-tetrahedron, $\Psi$. The relative volume of the simplex, $SSD_m$, is calculated as
a ratio of $SSD_n$ with respect to $SSD_u$ in order to compensate for the effect of dimensionality. This is because of the reduction in the volume of a unit tetrahedron by increasing its dimensionality. In fact, $SSD_m$ coefficients are equivalent to those of the Gram-matrix method, but scaled by the unit hyper-tetrahedron.

The normalized volume of the simplex in each step is also an appropriate metric to specify the dominant primaries in the painting regardless of the length of the vectors. The extracted pigments in lower dimensions have more significant contribution to reproducing the variance of the data. In practice, the volume is calculated when the tetrahedron has at least three vertices. The $SSD_m$ was manually set to unity for the first and second dimensions since it is not calculated.

Note that the ID is different form the number of actual pigments specifically when the primary pigments are highly correlated. Accordingly, the results of ID algorithms depend on the nature of the primary pigments. The correlation of constituent primary pigments is more probable when the number of primaries increases. As a result, no certain methods function accurately for estimating the actual number of primary pigments in practice. However, for a better examination of the unmixing algorithms, the ID of the spectral images was set to the known number of primary pigments. Meanwhile, the recommendation for ID is provided in the results.

5.6 Database Comparison

The extracted endmembers are representative of a set of virtual pigments. The virtual primaries are applicable for visualizations, simulations and spectral reconstructions. However, identifying representative actual pigments is quite useful for treatments such as inpainting where actual pigments are involved. The database comparisons are also beneficial in extracting the pure elements when the extracted endmembers are mixtures of pure pigments. The database comparison together with the unmixing algorithms forms a powerful way of extracting pure elements. When there are no pure elements within the painting, the SGA indicates the pixels
that are not perfectly pure, but a sparse combination of fewer pure primaries. The database comparison specifies the best binary or ternary combinations of actual pigments that span the estimated endmembers. Meanwhile, the complexity of extracting the pure elements is reduced. A summary of the procedure is schemed in Figure 5.12.

![Figure 5.12: A scheme of the database comparison workflow.](image)

The comparison algorithm is based on the estimation errors and concentration sparsity of the extracted endmembers. The concentration sparsity was specified according to the estimated concentration for matching an endmember. If pure elements already exist within the exemplar pixels, a one-to-one comparison is sufficient for finding corresponding pure pigments. In this case, each endmember is treated independently (Figure 5.13). This method is beneficial for endmembers from the SPICE method where they are representative of pure elements.

![Figure 5.13: The process of one-to-one database comparison.](image)

When each of the extracted endmembers is the mixture of other primaries, the algorithm should select the pigment combination with the smallest spectral error and maximum sparsity for all the endmembers, simultaneously. Since comparing all
possible pigment combinations it is not possible, a limited numbers of pigments with small SAM value (in K/S space) were picked to make the combinations. The pigment set that generates the smallest RMS error (according to a distance function) for all the estimated endmembers is picked as the \textit{best spectral match} combination. For a particular combination, $D_i$, the upper endpoints of the 95% confidence interval, $D_i$, chosen as a final RMS error for a given pigment combination:

$$D_i = \bar{D}_i + 1.96 \frac{\sigma_{D_i}}{\sqrt{n}}$$

Eq. 5.10

The \textit{best sparse match} refers to the pigment combination that produces sparse concentrations with acceptable RMS error. Since extracted endmembers are assumed to be the pure constituent elements of the painting, the corresponding primary pigment must reproduce the element with a high amount of relative concentration. In other words, the estimated recopies for the endmembers must be sparse. The sparsity index can be defined as a metric of concentration for the chosen pigments. In the meantime, the chosen concentration sets must have reasonable spectral reproduction accuracy. Thus, a limited number of combination sets with reasonably small distance functions are chosen for sparsity evaluations. The sparsity index was defined similar to Eq. 5.10, but the distance function was replaced with the pigment concentration. Eventually, two combination sets with the maximum sparsity are selected for further evaluations. Figure 5.14 is a summary of multiple comparisons of endmembers and the pigment database.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure514.png}
\caption{The process of multiple database comparison.}
\end{figure}
A preliminary primary pool is obtained by extracting the best combination sets corresponding to the unmixing methods and predefined dissimilarity functions. The dissimilarity function can be in either spectral reflectance or K/S space. Two dissimilarity functions, L2 and SAM, were chosen due to their popularity, simplicity and performance (Section 2.7.2). The dissimilarity functions were applied in the K/S and spectral reflectance spaces. The ΔE*94 is a perceptual-based metric to extend the assessments to perceptual sensations. ΔE*94 was selected over CIEDE2000 color difference formula due to its reasonable processing time. Each of the SGA and SPICE unmixing algorithms were examined for unknowns and a predefined white component. The unmixing algorithms with predefined white are denoted by the “+” superscript. A factorial combination of possible cases leads to a preliminary pool of 80 combination candidates (Table 5.1).

<table>
<thead>
<tr>
<th>Distance Function</th>
<th>Spectral Space</th>
<th>Objective</th>
<th>No. of Combinations</th>
<th>Unmixing Algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>Spectral Reflectance</td>
<td>RMS error</td>
<td>Single Combination</td>
<td>SGA + Predefined white (SGA+)</td>
</tr>
<tr>
<td>SAM</td>
<td>K/S</td>
<td>Sparsity</td>
<td>All Pigment Combination</td>
<td>SGA + Extracted White</td>
</tr>
<tr>
<td>ΔE*94</td>
<td>K/S</td>
<td></td>
<td></td>
<td>SPICE +Predefined white (SPICE+)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SPICE +Extracted white</td>
</tr>
</tbody>
</table>

Next, the candidate combinations are used to estimate the spectral reflectance of a set of new exemplar pixels from the image using 2-KM theory. As opposed to the previous dataset, the selected pixels contain a full representation of the image, including dark and light pixels. Therefore, the primary pigments are indicated by scattering and absorption properties. The goal is to find the pigment set that characterizes the dark and light colors of the painting. Therefore, the scattering of the mixtures becomes a significant factor for pigment selection in this step. Eventually, three sets of primary pigments are selected based on the smallest 90th percentile of reflectance RMS, K/S RMS and ΔE*94.

Note that an efficient spectral comparison requires a proper level of instrumental agreement. Geometric dissimilarities of spectral measurement devices can change the measured reflectance curvatures, which is particularly noticeable in (K/S) space.
Consequently, the geometric differences between the spectrophotometer used for pigment database and the spectral acquisition system were compensated using gray patches of ColorChecker Passport and the method explained in Chapter 3. Consequently, \( \mu \) and \( \rho \) parameters of Eq. 3.5 estimated by solving an over estimated set of equations for all the reflectances of gray patches measured by two spectrophotometers.

### 5.7 2-KM coefficient estimations

According to the results explained in Chapter 4, the estimated concentrations from the modified 1-KM can be used for calculating 2-KM coefficients. The concentration values can be calculated using Eq. 4.29 and a given impurity index. The impurity indices of the pigments were optimized as the result of repeating the coefficient estimations for different impurity indices and selecting those with maximum positive concentrations. The 2-KM coefficients were estimated using the second set of exemplar pixels that contain dark and saturated mixtures. Knowing the concentration values, the 2-KM coefficients were estimated using the least squares method with the reflectance-based weighting, explained in Eq. 4.1. The estimation can be limited to scattering coefficients by maintaining the estimated unit (k/s) as absorption coefficients as explained in Section 4.3.4; however, this approach did not improve the estimations in practice.

### 5.8 Pigment Identification Workflow

The process of pigment selection and concentration estimation, PI, was evaluated by considering a variety of parameters and unmixing combinations. The final workflow was obtained considering the final results for all the validation paintings (Figure 5.15). It should be noted that better results could be achieved by individual parameter adjustments for each painting.
Figure 5.15: The flowchart of pigment identification and concentration estimation process.

Below is a short description of each step specified in Figure 5.15:

1. The process begins with the spectral image from the LCTF acquisition system explained in Chapter 3.

2. The multispectral images are corrected for geometry dissimilarity to match to ColorEye-XTH spectrophotometer geometry using gray patches of
ColorChecker Passport as explained in Chapter 3. The Saunderson equation is applied to the spectral data for addressing the surface refractive index discontinuity. The Saunderson correction is recommended for concentration estimation when further comparisons to a pre-existing database are not performed. For pre-existing database comparisons, the Saunderson correction is skipped since the Saunderson coefficients cannot be accurately specified in the camera taking geometry. Next, the high-frequency content, containing uncharacterized spectral reflectances, is removed as explained in Section 6.2.

3-A uniform set of light and pale pixels are extracted using the spectral image from the previous step. The extracted pixels with acceptable CIE $C_{ab}^*$ and CIELAB $L^*$ are selected by maximizing the L2 spectral reflectance distance function (Section 6.2).

4-The spectral reflectance values of the uniform set of data are converted to K/S for dimensionality reduction. Principal component analysis (PCA) is used for dimensionality reduction as explained in Section 4.5. The PCA coefficients of the most significant eigenvectors corresponding to $\sim99.99\%$ cumulative eigenvalues are used for unmixing.

5- Three sets of pure pixels are extracted to be used for unmixing as explained in Section 6.1.1.

6- The proper path of unmixing algorithm is selected based on a preliminary knowledge about the white component in the paintings. If the white component is known SGA+ and SPICE+ are selected. If the white component is unknown regular SGA followed by SPICE algorithms are used, in which the white component is estimated separately.
7- PPI2 and PPI3 are used for the SGA unmixing method. The extracted endmembers following SGA are refined by a SA algorithm. The dimensionality of the data can be evaluated and reassigned by examining the volume of the normalized tetrahedron in successive increments of endmembers.

8- The endmembers from SGA are used as starting values for the SPICE algorithm. The sparse pure pixel set, PPI1, is used for optimizations.

9- The endmembers of SGA and SPICE are considered as intermediate estimations for pure elements. The extracted endmembers are used for pigment identification and concentration estimations in the next steps.

10- The endmembers of SGA- and SPICE-based methods are used for pigment comparisons. The endmembers are compared to the Okumura database as explained in Section 6.6. (The pigment database is already corrected to match the spectral properties of the camera, i.e., bandpass and wavelength scale.) The final pigment sets are extracted among a preliminary pool of primary candidates. The preliminary pigment pool is the result of comparing extracted endmembers to the pigment database. The final pigment sets that minimize the estimation error of a set of new exemplar pixels are selected from the preliminary pigment pool. The new exemplar pixels include dark and saturated colors.

11- The endmembers of the SPICE algorithm are used for 2-KM coefficient estimations and concentration maps. The 2-KM coefficients are derived based on the estimated concentrations using SPICE endmembers. Knowing k and s coefficients, the concentration maps of the entire spectral image are derived using 2-KM theory. The ID of the data can be verified by evaluating the RMS error images and concentration maps. If any of concentration maps contains zero values for the entire image, the actual dimensionality of the
image should be reduced. On the other hand, if a systematic RMS error is observed for a particular color, the ID should be increased. The pigment identification process should be repeated considering the new dimensionality number.

5.9 Experimental
The pigment identification algorithm was applied to 23 paintings with known constituent pigments as explained in Appendix E. the two major categories of pigment sets, old master and modern, were chosen for creating the validation paintings. Each category contained several paintings with a different number of primary pigments.

The spectral image of each painting was acquired by the capturing system explained in Chapter 3 and examined using the pigment identification algorithm. Okumura database, explained in Section 4.1.1.1, was also used for pigment comparisons. For comparisons of actual and predicted primary pigments see Appendices I and K. A summary of different error metrics are also provided in Appendix J.

5.10 Results and Discussion
A summary of the pigment identification of 23 spectral images is summarized in Table 5.2 and Table 5.3. In general, the algorithm yielded acceptable results specifically for the primary pigments with independent spectral curves, which led to reliable pigment identifications. The total percentage of correct predictions were 57.96%, 72.83% and 76.32% for $\Delta E^{*}$, reflectance RMS and K/S RMS metrics, respectively. The prediction rate was higher for the smaller number of primary pigments. Increasing the number of pigments added uncertainty to the predictions due to the correlation between constituent primaries. The dependency of the primary pigments also affected the estimation of the intrinsic dimensionality (ID). The estimated IDs were smaller than the actual number of utilized pigment for the
painting when the number of actual primaries increased. The estimated IDs were obtained by looking at the cumulative eigenvalues (with the threshold of \( \sim 99.99\% \) for the maximum upper limit) and the relative simplex volume diagram. The dimensionality of the data can be less than the actual number of primary pigments when the primaries are linearly dependent. For instance, the raw umber spectral shape can be closely replicated using carbon black, yellow ochre and titanium white. Incorrect dimensionality selection can be specified and corrected in the next steps of the PI and concentration estimations. In most cases the choice of unnecessary dimensionalities harmed the process of concentration and K/S estimations by adding extra dimensionality that led to singularity of the coefficient matrices. The singularity of the coefficient matrix can lead to negative and unreal predictions. The problem is more likely for a larger number of primaries because the estimated primary pigments have more chance to be linearly dependent. A practical solution for matrix singularity is to repeat the calculations for a combination of fewer primaries and select the best spectral match. For instance, in the case of seven primary pigments, all combinations of six pigments were utilized for a spectral match. Eventually, the combination with the smaller RMS error was picked as the final answer. The non-negative least square method is another alternative that usually enhances the predictions, but is computationally expensive.
Table 5.2: The database pigment comparisons for Old Master validation paintings.

<table>
<thead>
<tr>
<th>Painting</th>
<th>Actual Pigments</th>
<th>ΔE°*94</th>
<th>Database Comparison</th>
<th>K/S RMS</th>
<th>ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1-1</td>
<td>Red Oxide</td>
<td>Red Oxide Hansa Yellow Ultramarine Blue (2/3)</td>
<td>Red Oxide Yellow Ochre Ultramarine Blue (3/3)</td>
<td>Red Oxide Raw Sienna Ultramarine Blue (2/3)</td>
<td>4±1</td>
</tr>
<tr>
<td>1-1-2</td>
<td>Red Oxide</td>
<td>Red Oxide Hansa Yellow Payne’s Gray (1/3)</td>
<td>Red Oxide Yellow Ochre Ultramarine Blue (3/3)</td>
<td>Red Oxide Yellow Ochre Ultramarine Blue (3/3)</td>
<td>4±1</td>
</tr>
<tr>
<td>1-2-1</td>
<td>Red Oxide</td>
<td>Red Oxide Payne’s Gray Yellow Ochre Cobalt Blue (3/4)</td>
<td>Burnt Sienna Raw Umber Raw Sienna Cobalt Blue (2/4)</td>
<td>Red Oxide Carbon Black Yellow Ochre Cobalt Blue (3/4)</td>
<td>5±1</td>
</tr>
<tr>
<td>1-2-2</td>
<td>Red Oxide</td>
<td>Red Oxide Raw Umber Yellow Ochre Ultramarine Blue (4/4)</td>
<td>Red Oxide Carbon Black Raw Sienna Ultramarine Blue (2/4)</td>
<td>Red Oxide Yellow Ochre Ultramarine Blue (4/4)</td>
<td>5±1</td>
</tr>
<tr>
<td>1-3-1</td>
<td>Carbon Black</td>
<td>Anthraquinone Blue Red Oxide Burnt Sienna Yellow Ochre Hansa Yellow Ultramarine Blue (1/5)</td>
<td>Carbon Black Red Oxide Titan Buff Yellow Ochre Diarylide Yellow Ultramarine Blue (4/5)</td>
<td>Carbon Black Yellow Ochre Diarylide Yellow Ultramarine Blue (4/5)</td>
<td>5±1</td>
</tr>
<tr>
<td>1-3-2</td>
<td>Carbon Black</td>
<td>Carbon Black Red Oxide Naphthol Red Hansa Yellow Medium Ultramarine Blue (3/5)</td>
<td>Carbon Black Red Oxide Naphthol Red Yellow Ochre Ultramarine Blue (4/5)</td>
<td>Carbon Black Yellow Ochre Ultramarine Blue (4/5)</td>
<td>4±5</td>
</tr>
<tr>
<td>1-4-1</td>
<td>Chromium Oxide Green</td>
<td>Chromium Oxide Green Burnt Sienna Carbon Black Burnt Umber Diarylide Yellow Payne’s Gray (2/6)</td>
<td>Chromium Oxide Green Burnt Sienna Carbon Black Raw Sienna Diarylide Yellow Payne’s Gray (2/6)</td>
<td>Quinacridone Crimson Raw Sienna Carbon Black Yellow Ochre Diarylide Yellow Payne’s Gray (2/6)</td>
<td>5±1</td>
</tr>
<tr>
<td>1-4-2</td>
<td>Chromium Oxide Green</td>
<td>Chromium Oxide Green Red Oxide Carbon Black Raw Umber Yellow Ochre Diarylide Yellow Ultramarine Blue (6/6)</td>
<td>Chromium Oxide Green Red Oxide Carbon Black Raw Sienna Diarylide Yellow Payne’s Gray (3/6)</td>
<td>Chromium Oxide Green Red Oxide Carbon Black Raw Umber Yellow Ochre Diarylide Yellow Ultramarine Blue (6/6)</td>
<td>6±1</td>
</tr>
<tr>
<td>Painting</td>
<td>Actual Pigments</td>
<td>( \Delta E^* )</td>
<td>Database Comparison</td>
<td>K/S RMS</td>
<td>ID</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>----------------</td>
<td>-------------------</td>
<td>---------</td>
<td>----</td>
</tr>
<tr>
<td>1-5-1</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Chromium Oxide Green Red Oxide Carbon Black Hansa Yellow Medium Quinacridone Crimson Diarylside Yellow Ultramarine Blue (4/7)</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Hansa Yellow Medium Quinacridone Crimson Diarylside Yellow Ultramarine Blue (5/7)</td>
<td>Chromium Oxide Green Red Oxide Carbon Black Hansa Yellow Medium Quinacridone Crimson Diarylside Yellow Ultramarine Blue (4/7)</td>
<td>5-6</td>
</tr>
<tr>
<td>1-5-2</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Hansa Yellow Medium Red Oxide Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue (5/7)</td>
<td>Chromium Oxide Green Raw Umber Yellow Ochre Burnt Sienna Quinacridone Crimson Diarylside Yellow Payne’s Gray (4/7)</td>
<td>Hansa Yellow Medium Red Oxide Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue (6/7)</td>
<td>5-6</td>
</tr>
<tr>
<td>1-5-3</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Chromium Oxide Green Burnt Sienna Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue (6/7)</td>
<td>Chromium Oxide Green Raw Sienna Carbon Black Yellow Ochre Quinacridone Crimson Diarylside Yellow Ultramarine Blue (4/7)</td>
<td>Chromium Oxide Green Burnt Umber Raw Umber Yellow Ochre Pyrrole Red Diarylside Yellow Ultramarine Blue (6/7)</td>
<td>5-6</td>
</tr>
<tr>
<td>1-6-1</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Cobalt Blue Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Hansa Yellow Medium Red Oxide Carbon Black Burnt Umber Hansa Yellow Pyrrole Red Diarylside Yellow Payne’s Gray (3/8)</td>
<td>Hansa Yellow Medium Red Oxide Carbon Black Burnt Umber Hansa Yellow Pyrrole Red Diarylside Yellow Payne’s Gray (3/8)</td>
<td>Hansa Yellow Medium Red Oxide Carbon Black Hansa Yellow Quinacridone Crimson Diarylside Yellow Payne’s Gray (2/8)</td>
<td>5-6</td>
</tr>
<tr>
<td>1-6-2</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Cobalt Blue Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Chromium Oxide Green Red Oxide Titan Buff Turquoise Hansa Yellow Medium Quinacridone Crimson Diarylside Yellow Cezanne Blue (3/8)</td>
<td>Chromium Oxide Green Red Oxide Titan Buff Hansa Yellow Medium Quinacridone Crimson Diarylside Yellow Turquoise (4/8)</td>
<td>Chromium Oxide Green Red Oxide Titan Buff Hansa Yellow Medium Cobalt Blue Quinacridone Crimson Diarylside Yellow Turquoise (4/8)</td>
<td>6±1</td>
</tr>
<tr>
<td>1-6-3</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Cobalt Blue Pyrrole Red Diarylside Yellow Ultramarine Blue</td>
<td>Chromium Oxide Green Anthraquinone Blue Cobalt Blue Yellow Ochre Diarylside Yellow Red Oxide Quinacridone Crimson (5/8)</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Cobalt Blue Quinacridone Crimson Diarylside Yellow Ultramarine Blue (7/8)</td>
<td>Chromium Oxide Green Red Oxide Raw Umber Yellow Ochre Cobalt Blue Quinacridone Crimson Diarylside Yellow Ultramarine Blue (7/8)</td>
<td>5-6</td>
</tr>
</tbody>
</table>

Correct Predictions 66.01% 67.43% 76.15%
Table 5.3: The database pigment comparisons for modern validation paintings.

<table>
<thead>
<tr>
<th>Painting</th>
<th>Actual Pigments</th>
<th>$\Delta E^*_{ab}$</th>
<th>Database Comparison</th>
<th>K/S RMS</th>
<th>ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1-1</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue (3/4)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue (4/4)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue (3/4)</td>
<td>5±1</td>
</tr>
<tr>
<td>2-1-2</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Pyrrole Red</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Payne’s Gray (3/4)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue (4/4)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue (3/4)</td>
<td>4±1</td>
</tr>
<tr>
<td>2-2-1</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Pyrrole Red</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (4/6)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (4/6)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (4/6)</td>
<td>6±1</td>
</tr>
<tr>
<td>2-2-2</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Pyrrole Red</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (5/6)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (5/6)</td>
<td>Quinacridone Magenta, Hansa Yellow, Cobalt Blue, Ultramarine Blue, Phthalo Blue, Quinacridone Crimson (5/6)</td>
<td>6±1</td>
</tr>
<tr>
<td>2-3-1</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3/3)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3/3)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3/3)</td>
<td>6±1</td>
</tr>
<tr>
<td>2-3-2</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3/4)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (4/4)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (4/4)</td>
<td>4±1</td>
</tr>
<tr>
<td>2-7-2</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow, Pyrrole Red, Phthalo Green, Carbon Black</td>
<td>Phthalo Blue, Naphthol Red, Hansa Yellow Medium, Quinacridone Crimson, Phthalo Green, Payne’s Gray (2/6)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow Medium, Quinacridone Crimson, Phthalo Green, Ultramarine Blue (4/6)</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow Medium, Quinacridone Crimson, Phthalo Green, Ultramarine Blue (4/6)</td>
<td>5-6</td>
</tr>
<tr>
<td>2-8-1</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow, Pyrrole Red, Phthalo Green, Carbon Black, Diarylide Yellow</td>
<td>Phthalo Blue, Naphthol Red, Hansa Yellow Medium, Quinacridone Crimson, Cerulean Blue, Burnt Umber, Diarylide Yellow (2/7)</td>
<td>Phthalo Blue, Quinacridone Crimson, Hansa Yellow Medium, Quinacridone Crimson, Cerulean Blue, Titan Buff, Diarylide Yellow (3/7)</td>
<td>Phthalo Blue, Quinacridone Crimson, Hansa Yellow Medium, Quinacridone Crimson, Cerulean Blue, Raw Sienna, Diarylide Yellow (3/7)</td>
<td>5-6</td>
</tr>
</tbody>
</table>
The, spectral reflectance and K/S RMS error metrics led to reliable predictions for pigment selection. One drawback of spectral reflectance-based metrics was the difficulties of calculating the spectral reflectance from estimated K/S, particularly for bright and red colors, where the spectral values are close to 100%. In such instances, K/S matches with negative values lead to imaginary spectral reflectance value. The imaginary number can be avoided using clipping or non-negative least square methods, but the estimated reflectance might not be matched accurately. An example of an inaccurate prediction for a yellow primary will be discussed in Section 5.11.1.1.

The Saunderson surface correction should be applied to the spectral data prior to PI, even though it is not recommended for pigment selection unless the Saunderson coefficients are derived accurately for different geometries. The Saunderson correction, using recommended internal and external refractive index coefficients, scales and shifts the measured spectral reflectance towards higher values, which intensified the sensitivity of spectral matches specifically for light shades. Thus, small noise level or miscalculations of Saunderson coefficients cause significant inter-instrument disagreements. On the other hand, specifying the exact Saunderson coefficients for camera-taking geometries is not an easy task. The surface structure of the painting is an example of possible differences of Saunderson coefficients for a constant set of pigments and a single capturing geometry. Using measured spectral reflectance, as opposed to internal spectral reflectance, is recommended particularly for concentration and database comparisons due to the more stable results.
The functionality of the pigment selection algorithm relies on several factors. The most important factor is the dependency of the constituent pigments. The primary pigments that can have a spectral replication using other primaries are not considered as independent primaries mathematically, even though they might be a separate primary pigment physically. For example, the spectral shape of the carbon black pigment can be replicated by other primaries when the number of primaries is large. Notice that the black pigment was not identified in the paintings 2-7-2, 2-8-1 and 2-8-2. The black and raw umber could not be completely identified in paintings 1-3-1 and 1-3-2 for the same reason. On the other hand, pigments with unique curvatures, such as diarylide yellow, chrome oxide green, phthalo blue, hansa Yellow and phthalo green were extracted correctly in most cases.

Okumura’s database comprises of a variety of artist pigments, some of which are highly correlated. For instance, yellow ochre and raw sienna have very similar curves as shown in Figure 5.16 and Figure 5.17. Notice that these two pigments are hardly distinguishable even when pure mixtures are used in the painting. The CIELAB values of mixtures of yellow ochre and raw sienna are shown in Figure 5.17. Note that the hue angles of the two pigments are quite close. The differences are more difficult to specify in the presence of another pigment such as red oxide. For instance, a mixture of yellow ochre and red oxide can lead to a reasonable replication of raw sienna as shown in Figure 5.17. Note that the CIELAB color gamut of yellow ochre and red oxide is similar to that of yellow ochre, red oxide, and raw sienna. Likewise, other pigment pairs such as ultramarine blue (for pale shades) and payne’s gray and red oxide and burnt sienna can be confused. Another example is the discrimination of pyrrole red and quinacridone crimson with similar spectral shapes, which requires more precise spectral measurements for spectral separations. For further spectral comparisons of Okumura’s database, see Appendix K.
Figure 5.16: Spectral reflectance and K/S values of yellow ochre and raw sienna pigments.

Figure 5.17: CIELAB values of yellow ochre, raw sienna and red oxide ramps. a) CIELAB values of individual ramps. b) CIELAB values of the mixtures of red oxide, yellow ochre and white pigments. c) CIELAB values of mixtures of ochre, raw sienna, red oxide pigments and white.

The image contents also influence the process of pigment identifications. Clearly, images that merely include dark and extremely saturated colors (such as paintings 2-8-2 and 1-6-1) or high frequency (such as paintings 1-4-1 and 1-1-2) contents do not provide enough samples for pigment identification. Both categories of dark and
high frequency contents are removed in the exemplar selection step. However, most of the regular images have sufficient numbers of eligible pixels.

The SGA-based unmixing algorithm led to better comparison results than SPICE. Consequently, a combination of the SGA method and pigment detection workflow is recommended for pigment comparisons. The SPICE algorithm is preferred for concentration estimations and when no database of the pure elements is available. The extracted endmembers represent pure element so they are suitable for simulations and visualizations. Although the extracted endmembers may be a reasonable estimation of actual pigments, more realistic evaluations require a pre-existing database.

5.11 Case Study

The process of PI requires different considerations for each specific painting; however, the parameters and workflow of PI were specified for further comparisons. Four spectral paintings were chosen for further evaluations of each step of PI. Two images with four primary pigments plus white from modern palettes were chosen for general evaluation of different steps. Two other paintings were chosen from old master paintings with eight primary pigments plus white as extreme cases. The Saunderson geometry correction was skipped due to uncertainties in Saunderson coefficients for the two different geometries.

5.11.1 Modern Four-Pigment

Two paintings were made up of four primary pigments plus white with codes 2-1-1 and 2-1-2 from Table E.2. The paintings contained two blue pigments with different spectral shapes. Each of the paintings are evaluated in separate sections as follows:

5.11.1.1 The Four-Pigment Modern Palette

A colorimetric rendering of the original image is shown in Figure 5.18. Three steps of exemplar pixel selections are demonstrated in Figure 5.19. A down-sampled CIELAB color gamut of the image is also plotted. The selected exemplar pixels were passed to the dimension reduction step.
Figure 5.18: A rendering of the spectral image 2-1-2 for 2° observer and D65 illuminant. The painting is made of cobalt blue, hansa yellow, quinacridone magenta, ultramarine blue pigments and white.

Figure 5.19: Renderings of the spectral of image and corresponding CIELAB plot after filtration (top) and exemplar selection (bottom). The images are rendered for 2° observer and D65 illuminant.

The results of PCA analysis of the exemplar pixels are shown in Figure 5.20. A simple threshold-based method suggests five eigenvectors for characterization of ~99.99% of the variations even though only four primary pigments were used for creating the painting. As already explained, the final dimensionality of the data is
specified after performing the geometry method. However, for this example the number of primary pigments was maintained at five.

Figure 5.20: PCA eigenvalues (left) and five most significant eigenvectors (right) of the exemplar pixels.
Figure 5.21: 3D plots of PCA coefficients of exemplar pixels. In each plot, the black circles identify selected pure pixels.
The estimations of SGA in each iteration are shown in Figure 5.22. The extracted endmembers can be ordered according to their contribution to form the simplex with the maximum volume. In this example, adding the fourth endmember was as significant as the third vector. However, the fifth endmember did not increase the simplex volume considerably (Figure 5.23). In other words, the fifth vector was a linear combination of previously selected primaries. The increase in the simplex volume can be due to measurement noise at long wavelengths. The dimensionality of the data can be readjusted in this step and then restart the PI workflow.
First iteration

Second iteration

Third iteration

Figure 5.22: Extracted endmember in each iteration using SGA.
Figure 5.23: The volume of the unit simplex in each iteration using SGA.

The extracted primaries were used as initial values of the SPICE method. The estimated endmembers using the SPICE technique are shown in Figure 5.24. The actual primary pigments (ultramarine blue, cobalt blue, hansa yellow and quinacridone magenta) were extracted correctly. The fifth primary has an unrealistic shape since it does not represent any actual pigment.

Figure 5.24: Extracted endmembers in K/S (left) and spectral reflectance (right) spaces using SPICE. The algorithm applied with (top) and without (bottom) a predefined white component. The predefined white component is titanium white.
Considering Figure 5.23, the fifth endmember led to a small increase in the simplex volume. It means that the fifth endmember provided redundant information and can be replicated as a linear combination of previously selected primaries. Accordingly, the algorithm was repeated but for four primary pigments rather than five. It should be remembered that the simplex volume is influenced by the spectral properties of the primary pigments. However, more accurate ID verification needs to be performed by evaluating the RMS error images using the final primary pigments. The estimations of SGA and SPICE for four primaries are shown in Figure 5.25. Comparing the results of five and four primary pigments, estimated endmembers for actual pigments remained the same.

![Extracted endmembers using SGA (left) and SPICE (right) with ID of four. The algorithms applied with (top) and without (bottom) a predefined white component.](image)

The next step is to compare the extracted endmembers to the pigment database. The algorithm determines the best pigment match based on the assigned dissimilarity
function. A summary of database comparisons is shown in Table 5.4. The largest errors belonged to the SPICE method with minimum ΔE°94 when the white component was not fixed. Clearly, minimizing ΔE°94 does not guarantee the best spectral match since it might lead to metameric matches. Other methods yielded a correct estimation for ultramarine blue, quinacridone magenta and hansa yellow. The cobalt blue pigment was identified as cerulean blue in several methods when K/S values were minimized. The reason can be addressed by considering Figure 5.27. Notice that the K/S curves of cobalt blue and cerulean blue pigments are quite similar in K/S space; therefore, estimated and actual spectral matches have small K/S RMS values. These small spectral differences can be compensated by other primary pigments, which resulted in a wrong pigment selection. Note that the error metrics for different pigment sets shown in Table 5.4 are rather small. These differences become even more negligible when larger numbers of primary pigments are involved. This is an actual limitation of spectral-based pigment identification when different combinations of database primaries can replicate the extracted primaries. Extending the spectral measurement wavelength range is an approach to provide more spectral information usable for better separations. Figure 5.26 is a plot of cobalt blue and cerulean blue pigments that are usually difficult to distinguish in the spectral range of the current LCTF-based acquisition system. Note that light shades of either of the pigments have rather similar spectra leading to more challenging PIs. However, extending the spectral measurements towards the IR and UV yields more information for PI. In this figure, the red area identifies the wavelength range measured by the LCTF-based acquisition system and the green areas correspond to possible expansions of the spectral measurements. Note that the expansion in into the short wavelength region can provide critical information for distinguishing the pigments.
Figure 5.26: spectral reflectances of cobalt blue (left) and cerulean blue (right) ramps. Red area corresponds to the spectral range measured by LCTF-based acquisition system. The green areas correspond to the possible extensions of spectral measurements for more accurate pigment identifications.
Table 5.4: The results of database comparison for pigment identification for painting No. 2-1-2. Superscript + refers to the methods in which the white component is predefined. Correct estimations are in bold.

<table>
<thead>
<tr>
<th>Method</th>
<th>Best Match</th>
<th>(\Delta E^*_{94})</th>
<th>90th KM RMS</th>
<th>90th Reflectance RMS</th>
<th>90th (\Delta E^*_{94})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPICE</td>
<td>Turquois Ultramarine Blue</td>
<td>0.2457</td>
<td>0.0805</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Naphthol Red</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow Medium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Ultramarine Blue</td>
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<td>0.0294</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPICE+</td>
<td>Ultramarine Blue</td>
<td>0.1219</td>
<td>0.0255</td>
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</tr>
<tr>
<td></td>
<td>Cerulean Blue</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
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<tr>
<td></td>
<td>Hansa Yellow</td>
<td></td>
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<tr>
<td>SPICE+</td>
<td>Ultramarine Blue</td>
<td>0.1219</td>
<td>0.0255</td>
<td>1.8</td>
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<tr>
<td></td>
<td>Cerulean Blue</td>
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<tr>
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<td>Quinacridone Magenta</td>
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<td></td>
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<td></td>
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<tr>
<td></td>
<td>Hansa Yellow</td>
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<td></td>
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</tr>
<tr>
<td>SGA</td>
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</tr>
<tr>
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<td></td>
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<td></td>
<td>Hansa Yellow</td>
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</tr>
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<td></td>
<td>Cobalt Blue</td>
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<td></td>
<td></td>
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<td>Quinacridone Magenta</td>
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<td></td>
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<tr>
<td></td>
<td>Hansa Yellow</td>
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<tr>
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<td>0.0255</td>
<td>1.8</td>
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<tr>
<td></td>
<td>Cerulean Blue</td>
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<tr>
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<td>Quinacridone Magenta</td>
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<td></td>
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<td></td>
<td>Hansa Yellow</td>
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<td>Cobalt Blue</td>
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<td>Quinacridone Magenta</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

The measurement accuracy for small reflectance values (~610nm) was also considerable in this case (Figure 5.27). Even though the spectral reflectances were rather similar, the K/S shapes had noticeable differences. Obviously, any improvement in spectral measurement can be a remedy for this problem. Using spectral based metrics is a solution to eliminate the sensitivity of the pigment selection to the measurement noise in K/S space.
Figure 5.27: Spectral curves of the blue primary of SPICE algorithm (starred line) along with cerulean blue (right column) and cobalt blue (left column) pigments in spectral reflectance (top row) and K/S (bottom row) spaces.

None of the utilized error metrics are completely perfect for spectral comparisons. The spectral match for hansa yellow primary, shown in Figure 5.28 and Figure 5.29, is an example where reflectance RMS is not an appropriate error metric. Hansa yellow pigment has small absorption in long wavelength leading to small K/S values. The endmember estimations from SPICE are the result of K/S RMS minimizations after dimensionality reduction and with the positivity constraint. Consequently, the estimated spectra will be inaccurate for very small quantities. The small differences in K/S turn to large reflectance RMS errors in reflectance space, which resulted in large spectral reflectance RMS errors. The spectral match for hansa yellow primary using SGA+ is shown in Figure 5.29. The spectral RMS errors in reflectance and K/S spaces are smaller since the estimated endmembers are actual measurements.
The next step is to estimate 2-KM absorption and scattering coefficients according to the estimated concentrations. Estimations of 2-KM unit k and s coefficients for two sets of endmember sets are shown in Figure 5.30, which is comparable to those calculated using independent ramps. The endmembers of SGA methods were not for spectral and concentration estimations because they are not representative of the pure elements. The RMS errors of spectral estimations for the given image are illustrated in Figure 5.31. Large RMS errors corresponded to the masstones and dark mixtures that cannot be characterized by 2-KM theory. The RMS errors for saturated yellow samples are due to the small K/S values of the yellow pigments as mentioned above. Finally concentration maps of different pigments can be obtained according to calculated unit k and s (Figure 5.32). The correlation between concentration maps of 2-KM (using actual constituent pigments) and SPICE
unmixing estimations revealed the application of extracted endmembers even without the database comparison.

Figure 5.30: 2-KM unit k (solid lines) and s (dashed lines) coefficient estimations using different unmixing methods.
Figure 5.31: RMS errors of actual and estimated image in spectral reflectance space (left) and K/S space (right) for different methods.
Figure 5.32: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration maps on the right correspond to the concentration estimations using the 2-KM theory and actual primary pigments.
The overall prediction errors are provided in Table 5.5. Note that the RMS errors of the unmixing endmembers are comparable to those of 2-KM.

<table>
<thead>
<tr>
<th>Method</th>
<th>Mean</th>
<th>STD</th>
<th>Max</th>
<th>90th</th>
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<td></td>
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</tr>
<tr>
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<td>1.0</td>
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<tr>
<td>SPICE'</td>
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<td>11.8</td>
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</tr>
<tr>
<td>2-KM</td>
<td>0.8</td>
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</tr>
<tr>
<td>Reflectance RMS</td>
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</tr>
<tr>
<td>SPICE</td>
<td>0.0219</td>
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<tr>
<td>2-KM</td>
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<td>0.2310</td>
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<tr>
<td>K/S RMS</td>
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<td></td>
<td></td>
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<tr>
<td>SPICE</td>
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<td>SPICE'</td>
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</table>

5.11.1.2 The Four-Pigment Modern Painting

The process of pigment identification can be more complicated for real paintings where the existence of pure elements or the white element is not certain. Figure 5.33 is a render of a painting comprised of four primary pigments. The painting does not include pure pigments or a white component.

![Figure 5.33: A render of the spectral image 2-1-2 for 2° observer and D65 illuminant. The painting is made of cobalt blue, hansa yellow, quinacridone magenta and ultramarine blue pigments.](image)
The dimensionality of the data was chosen as four according to prior knowledge of the painting. PCA cumulative eigenvalues and the simplex volume plot (Figure 5.34) also suggest the dimensionality of four or five. The extracted primaries of the different methods are shown in Figure 5.35. For this painting, the extracted endmembers are mixtures of actual primaries. Consequently, a one-to-one comparison of each endmember and the actual pigments of the database cannot be used for an effective pigment selection. The SGA+ endmembers and a spectral match with the actual pure pigments are shown in Figure 5.36. The spectral estimation error revealed that the extracted endmembers were actually a mixture of primary elements. In this case, the database comparison algorithm examined the endmembers by examining the multiple combination of primary pigments.

Figure 5.34: The volume of the simplex in each iteration using SGA+ (left) and eigenvalues of PCA (right).
Figure 5.35: Extracted endmembers using SGA (left) and SPICE (right). The algorithms applied with (top) and without (bottom) a predefined white component.
Figure 5.36: Spectral matches of actual primary pigments (solid line) of the extracted endmembers (starred line) extracted by SGA+ algorithm using the SAM dissimilarity function.
The results of database comparison algorithm are summarized in Table 5.6. The issue of mismatching cerulean blue and cobalt blue pigments for the best $\Delta E_{94}$ and K/S RMS was repeated due to the same reason explained above. The spectral match was still accurate even though the chosen actual pigments were not exactly the same. The RMS error images for different pigment identification algorithms are shown in Figure 5.37. The largest K/S estimation errors belonged to very dark and saturated regions and edges.

Figure 5.38 is a demonstration of concentration maps of the SPICE* and SPICE methods. The concentration maps of both methods are rather similar to the concentrations estimated by the 2-KM algorithm as the ground truth implied reasonable pigment identification.

Table 5.6: The results of database comparison of extracted endmembers for painting No. 2-1-1. Correct estimations are in bold.

<table>
<thead>
<tr>
<th>Best Match</th>
<th>Indicated Pigments</th>
<th>$90^{th} \Delta E_{94}$</th>
<th>$90^{th}$ Reflectance RMS</th>
<th>$90^{th}$ K/S RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{94}$</td>
<td>Cerulean Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow</td>
<td>1.8</td>
<td>0.0254</td>
<td>0.1210</td>
</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultramarine Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K/S RMS</td>
<td>Cerulean Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow</td>
<td>1.8</td>
<td>0.0254</td>
<td>0.1210</td>
</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultramarine Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflectance RMS</td>
<td>Cobalt Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow</td>
<td>1.9</td>
<td>0.0242</td>
<td>0.1219</td>
</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultramarine Blue</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.37: RMS errors of spectral reflectance (left) and K/S curves (right) for different pigment identification methods.
<table>
<thead>
<tr>
<th>Reproduced Image</th>
<th>cobalt blue</th>
<th>hansa yellow</th>
<th>quinacridone magenta</th>
<th>ultramarine blue</th>
</tr>
</thead>
</table>

Figure 5.38: Concentration maps corresponding to the SPICE (left) and SPICE+ method (middle). The concentration map on the right corresponds to the concentration estimations using the 2-KM theory and actual primary pigments.
5.11.2 Eight-Pigment Old Master

Old master pigments are not as bright as the modern sets. Most of the old paints have smoother spectral shapes that affect the ID of the data and Pl performance. For a large number of primary pigments, different primary combinations can lead to reasonable spectral replications of the painting. Therefore, exact pigment identification is more challenging. Two paintings comprised of eight old-master primary pigments are examined in the following section.

5.11.2.1 The Palette

A colorimetric render of the palette painting is shown in Figure 5.39. Even though extracting eight primary pigments is relatively more difficult, existence of pure and white elements eased the identification algorithm for this painting.

![Figure 5.39: A render of the spectral image 1-6-3 for 2° observer and D65 illuminant. The painting is made of eight primary pigments: yellow ochre, red oxide, ultramarine blue, raw umber, diarylide yellow, chromium oxide green, pyrrole red and cobalt blue.](image)

The ID of the data was selected as eight based on the knowledge about the painting. However, the algorithm suggests at most seven independent signatures. The eighth primary might add negligible information for pigment identification.
Figure 5.40: The volume of the simplex in each iteration using SGA+ (left) and eigenvalues of PCA (right).

The sequence of endmembers selected for SGA+ algorithm is plotted in Figure 5.41. Even though ~100% of the variation can be characterized by six endmembers, a new primary in each iteration corresponds to an actual pigment. The final estimated endmembers for SGA+, SGA, SPICE+ and SPICE are potted in Figure 5.42.
Figure 5.41: Extracted endmembers in each iteration using SGA*.
Figure 5.42: The extracted endmembers using SGA, SGA, SPICE and SPICE*. The dashed lines indicate the white component.

The best pigment combinations for each error metric along with the RMS errors are shown Table 5.7. There are five pigments that are detected correctly regardless of the error metric. The best ΔE*94 estimation does not address black or raw umber pigments since they can be reproduced by other pigments colorimetrically. When the number of primary pigments gets large, the estimation errors are relatively small for most of the combinations. Generally, pigment sets that contain the chosen five pigments led to rather similar RMS errors.
The RMS error and concentration maps are shown in Figure 5.43 and Figure 5.44. Because of a larger number of degrees of freedom, the spectral estimations were rather small compared to the four-pigment paintings. Likewise, the large estimation K/S errors corresponded to the dark mixtures and masstrokes, and the large reflectance estimation belonged to the yellow and saturated red areas. The concentration maps of SPICE-based methods had a reasonable correlation with actual pigment concentrations calculated by 2-KM. In other words, the estimated endmembers were correct representatives of the actual pigments.
Figure 5.43: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
<table>
<thead>
<tr>
<th>Reproduced Image</th>
<th>Cobalt Blue</th>
<th>Yellow Ochre</th>
<th>Diarylide Yellow</th>
<th>Ultramarine Blue</th>
<th>Red Oxide</th>
<th>Chromium Oxide Green</th>
</tr>
</thead>
</table>

Figure 5.44: Concentration maps corresponding to the SPICE (left) and SPICE* method (middle). The concentration map on the right corresponds to the concentration estimations using the 2-KM theory and actual primary pigments.
1.1.1.1 Painting 1-6-1

The 1-6-1 painting with eight primary pigments was examined. A colorimetric rendering of the painting is shown in Figure 5.45. The painting was a complicated case in terms of pigment identification since different types of yellow and red pigments dominated the entire image. Most regions are solid and are made up of rather dark and saturated pigments with small amounts of mixture combinations. The blue background is a mixture of two blue pigments, which are difficult to distinguish. Additionally there are not a sufficient number of mixtures of pure pixels for SGA. Finally, there are no pixels of pure white in the image.
Both eigenvalue and simplex volume diagrams suggest no more than six independent signatures in the painting (Figure 5.46). The extracted endmembers of each method are plotted in Figure 5.47. The number of primary pigments is set to eight based on the knowledge of the painting. Most of the extracted endmembers are yellow, orange and red, resulting in considerable redundancy. The white is not estimated accurately in SGA and SPICE as shown in Figure 5.47. The extracted endmember consisted of yellow and red shades. Looking at the extracted endmembers, the best estimation belongs to the SGA method. The algorithm yielded a correct estimation of two blues, two yellows, two reds and the green pigments. The SGA+ method obtained a correct estimation of raw umber but missed the cobalt blue. The SPICE based algorithms did not produce accurate predictions because of the large number of primaries, which confirms the advantage of SGA-based algorithms when the number of primary elements is large and are mixtures of pure elements.
Figure 5.46: The volume of the simplex in each iteration using SGA (left) and eigenvalues of PCA (right).

Figure 5.47: The extracted endmembers using SGA*, SGA, SPICE and SPICE*. The dashed lines indicate the white component.

The results of database comparison are shown in Table 5.8. Red oxide, pyrrole red, and diarylide yellow were identified correctly by all the error metrics. The best reflectance pigment set gave a correct estimation of chromium oxide green, and the
ultramarine blue was identified as anthraquinone blue. The algorithm selected quinacridone magenta and hansa yellow medium for a better spectral match of the yellow and red pigments. The cobalt blue pigment and raw umber were identified in the best K/S match pigment set. The chromium oxide green pigment was reproduced by a mixture of ultramarine blue and other yellow and red pigments. Considering the RMS error images (Figure 5.48) the reconstructed image still has reasonable spectral accuracy. In this figure, 2-KM Recommended Pigments is the recommended recipe from the best spectral match from Table 5.8 (with the primary set of chromium oxide green, red oxide, anthraquinone blue, cobalt blue, pyrrole red, diarylide yellow, quinacridone magenta and hansa yellow medium). Even though the estimation error was fairly minor, the concentration maps were quite different and vague compared to those from 2-KM and actual pigments. Since the extracted endmembers are mixtures of actual pigments, calculated concentrations do not correspond to specific pigments. Despite the complexity of the pigment identifications for this painting, the concentration map for cobalt blue, diarylide yellow, red oxide, chromium oxide green, raw umber and pyrrole red still corresponded to the actual concentrations.
Table 5.8: The results of database comparison for pigment identification for painting No. 1-6-1. Correct estimations are in bold.

<table>
<thead>
<tr>
<th>Best Match</th>
<th>Indicated Pigments</th>
<th>90th $\Delta E^*_{94}$</th>
<th>90th Reflectance RMS</th>
<th>90th K/S RMS</th>
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</thead>
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<td></td>
<td>Red Oxide</td>
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<tr>
<td></td>
<td>Anthraquinone Blue</td>
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</tr>
<tr>
<td></td>
<td>Cobalt Blue</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>Pyrrole Red</td>
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<tr>
<td></td>
<td>Diarylide Yellow</td>
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<td>Quinacridone Magenta</td>
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</tr>
<tr>
<td></td>
<td>Hansa Yellow Medium</td>
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<tr>
<td>Reflectance RMS</td>
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<tr>
<td></td>
<td>Diarylide Yellow</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Quinacridone Magenta</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hansa Yellow Medium</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>0.4538</td>
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<tr>
<td></td>
<td>Raw Umber</td>
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<tr>
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<td>Pyrrole Red</td>
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<tr>
<td></td>
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<tr>
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<td>Ultramarine Blue</td>
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</tr>
<tr>
<td></td>
<td>Hansa Yellow Medium</td>
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</tbody>
</table>
Figure 5.48: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 5.49: Concentration maps corresponding to SPICE (left) and recommended actual pigments (middle). The concentration map on the right corresponds to the concentration estimations using 2-KM theory and actual primary pigments.
<table>
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<th>Reproduced Image</th>
<th>Anthraquinone Blue</th>
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<th>Anthraquinone Blue</th>
<th>Ultramarine Blue</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Red Oxide</td>
<td>Red Oxide</td>
<td>Red Oxide</td>
</tr>
<tr>
<td>Chromium Oxide-Green</td>
<td>Chromium Oxide-Green</td>
<td>Chromium Oxide-Green</td>
<td>Chromium Oxide-Green</td>
<td>Chromium Oxide-Green</td>
</tr>
</tbody>
</table>

Figure 5.49: Continued.
5.12 Conclusions

A spectral-image-based pigment identification workflow was introduced in this chapter. Two types of spectral unmixing algorithms were modified and applied to the 1-KM modified subtractive mixing model. The spectral unmixing algorithms were applied to the dimensionality-reduced data after a preliminary filtration of the spectral image. The filtration step provided a uniform and effective selection of pixels from the spectral image. The prior selection of primary pigments was used for a pigment determination algorithm with a pre-existing database of actual artist pigments. Eventually, the KM optical coefficients were extracted using the
previously estimated concentrations. The predicted coefficients were utilized for final concentration estimations of a number of validation paintings.

The spectral unmixing algorithms were applied on the PCA coefficients according to the estimated dimensionality of the data. The dimensionality of the data was determined in three steps of the algorithm. First, the intrinsic dimensionality (ID) was specified by assigning a threshold for the PCA eigenvalues. Next, the ID was evaluated and corrected by examining the simplex volume of SGA method in the sequences of adding endmembers. Finally, the ID was examined in the last step of pigment identification algorithm by evaluating the RMS error maps. It should be noted that specifying the ID depends on the number and the nature of the primary pigments making the ID determination algorithms a challenging problem.

Two spectral unmixing methods, SGA and SPICE, were modified for the endmember estimations with different applicability. The endmembers of the SGA method were selected from the spectral image; therefore, they were better choices for pigment selections from a database. On the other hand, the endmembers of SPICE-based methods were representative of pure pigments that were preferred for concentration estimations and visualizations.

The quality of the pigment identification and the endmember extraction relies on image content and the number and dependency of constituent primary pigments. The presence of the white and pure elements improved the estimations considerably for both the SGA and SPICE techniques. In contrast, image contents with small amounts of pigment mixtures, dark and saturated shades were more difficult cases for PI. The independency of primaries was found to be another significant factor. The linearly independent primary elements were identified with higher certainty and less confusion with other pigments.

The concentration and error images were metrics of overall performance of pigment identification. Comparisons of actual concentrations and those estimated using
extracted endmembers showed a reasonable correlation for most of the paintings. In other words, the endmember extracted from the SPICE methods were equivalent to the actual pigment primaries.
CHAPTER 6: IMPLEMENTATION FOR HIGH-RESOLUTION IMAGES

The preliminary knowledge of the primary pigments provides an effective tool for spectral and pigment concentration analysis from a multi-channel, high-resolution capturing system. The initial primary pigment data are provided by either the low-resolution spectral based pigment identification or other analytical techniques discussed in Chapters 5 and 2, respectively. For paint layers, the dimensionality of the spectral data can be lessened depending on the number of primary pigments. Theoretically, the dimensionality-reduced data can be related to the outputs of fast and relatively inexpensive multi-channel capturing systems rather than full-spectral measurements. This idea of extracting high-resolution spectral reflectance and concentration map images is summarized in Figure 6.1. As it is shown in the figure, there is no further image registration or image processing step is required, which is one significant advantage of the workflow.

The algorithm begins with a multi-channel, high-resolution image. Camera signals are converted to an intermediate spectral reflectance space by means of a uniform
training set simulated from the sensitivity of the capturing channels, SPD of the light source, and the pre-existing information of the primary pigments (Step 1).

Two training-based spectral reflectance methods were chosen for comparisons taking into account processing time and simplicity: 1) least-squares (R-LS), 2) Burns and Berns (1997) (R-PCA) methods. The basics and mathematical models of spectral reflectance algorithms were already explained in Section 2.4. The R-LS method relates the spectral reflectance and camera responses using a direct transformation matrix calculated for the existing training set. In the R-PCA method, the spectral reflectances are approximated by a linear combination of camera responses and a fewer number of coefficients corresponding to a series of basis functions describing the training data. The basis functions are the result of statistical analysis of the training set using a matrix factorization method such as principal component analysis (PCA). The transformation matrix is optimized to minimize the least squares error between camera responses and PCA coefficients using a direct regression. The number of significant basis functions is chosen according to the number of available independent camera channels to form a square transformation matrix (Burns and Berns, 1997). For more information of spectral reconstruction methods from fewer camera signals, review Section 2.4 and refs. (Ribés and Schmitt, 2008; Ribes, et al., 2008).

Once the spectral estimation method is specified, concentration maps can be extracted employing the spectral matching algorithm introduced by Walowit, et al., (1988) knowing the primary pigment information (Step 2). Theoretically, the pigment concentration maps carry a full description of the spectral reflectance for each pixel. As a result, estimated concentration maps can be utilized for spectral enhancements as explained by Zhao, et al., (2005a) (Step 3). The spectral estimations using the KM theory are termed as R-PCA-KM or R-LS-KM depending on the spectral estimation method.
Figure 6.1: General workflow of pigment concentration and spectral reflectance estimations for multispectral, high-resolution images.

6.1 Training Dataset

The training dataset is a collection of pigment concentrations and multi-channel camera responses that includes a reasonable number of primary combinations with a uniform distribution. The dataset was built by modulating the pigment concentrations for a variety of pigment combinations as shown in Figure 6.2.

Figure 6.2: The workflow of creating the training dataset.
The number of the concentration intervals should be selected carefully because all possible combinations of the primary pigments can easily lead to a large number of mixtures. One alternative of reducing the number of gridding points is to select the concentration intervals so that the resulted camera responses have a uniform distribution. A uniformly distributed dataset was derived by carefully adjusting the concentration intervals to earn equal Euclidian distances in CIELAB color space. For instance, the CIELAB values of a set of mixtures of phthalo blue pigment and titanium white pigments with equal concentration intervals are shown in Figure 6.3. The concentration intervals can be reassigned to get equal Euclidian distances in camera response space. Figure 6.4 is a plot of the relationship of the pigment concentration and cumulative Euclidian distances in camera response space. The new concentration intervals are selected to obtain equal Euclidian distances (filled dots in Figure 6.4). The CIELAB values of the new concentration sets are more uniformly distributed specifically in very dark and light concentration ranges as shown in Figure 6.5.

Figure 6.3: CIELAB L*-B* plot of mixtures of phthalo blue pigment and titanium white with equal concentration spacing.
The results of uniformly vs. adjusted concentration modulations for mixtures of three chromatic and white pigments are shown in Figure 6.6. Note that the total number of training points is similar for both cases; however, the adjusted concentration intervals covered the color space more appropriately.
6.2 High-Resolution Implementation

The process of spectral and concentration estimations can be applied to the high-resolution directly. However, error evaluations are not possible since there are no ground-truth high-resolution spectral images available. More advanced solution is to simulate a low-resolution version of the high-resolution image and perform a preliminary evaluations. For known sensor sensitivities and filter transmittances, the camera responses can be reasonably simulated from the LCTF spectral image. The simulated image is beneficial for pixel-by-pixel comparisons of the spectral reconstructions to those of LCTF without registration and down-sampling complexities. The approximation process for the Sinar camera was already verified by examining the correlation between the actual and simulated camera responses for a set of standard color patches as explained in (Berns and Wang, 2014).

The general workflow of spectral reconstruction and concentration estimations can be determined based on the quality of different reconstruction methods, PI, concentration and error maps from the simulated low-resolution image. The final spectral estimation workflow can be a combination of different methods leading to
the most reliable outputs. For instance, the KM-based spectral estimations can be used for light and non-saturated areas. Similarly, the R-LS or R-PCA–based algorithms can be applied where the KM theory is not valid. Eventually, the actual high-resolution spectral image is derived by extending the simulations to the high-resolution image from the six-channel camera system. A flowchart of the simulation pipeline is quite similar to Figure 6.1 but the multi-channel image is simulated from the LCTF spectral image as schemed in Figure 6.7.

![Figure 6.7: The workflow of pigment concentration and spectral reflectance estimations for simulated multi-channel images.](image)

### 6.3 Experimental

A six-channel measurement system (Dual-RGB) was used for image capturing. The capturing system included a 48-megapixel Sinarback, a rePro camera body, an eShutter electronic shutter with the ability of capturing two sets of high-resolution RGB images through two optimized blue and yellow filters (Berns, et al., 2005a; Imai and Berns, 2009). Two trichromatic images were captured in a sequence of time for two filters and using two Broncolor Pulso G-1600J sources in a 45:0 capturing geometry (Figure 6.8). The combination of camera RGB sensors and the filters results in a six-channel capturing system with the spectral sensitivity shown in
Figure 6.9 (Berns and Wang, 2014). The spectral sensitivity of the green channels are quite similar. Accordingly, the second green channel was removed from the calculations, which formed a five-channel acquisition system with more independent capturing channels.

Two paintings comprised of eight (with painting code 1-6-3 from Table E.1) and four (with painting code 2-1-2 from Table E.2) primary pigments mixed with titanium white were chosen for evaluation. The spectral images were measured with the LCTF-based multispectral acquisition system as explained in Chapter 3.
Finally, concentration maps and spectral reflectance of the paintings were estimated and compared for actual and estimated primary pigments.

6.4 Results and Discussion

6.4.1 Painting 2-1-2
The painting was comprised of two blue pigments plus yellow and magenta pigments plus white with codes 2-1-2 from Table E.2. Since the capturing system has five acquisition channels, this example can be considered an over-determined problem in which the number of primary pigments is smaller than the number of camera channels.

The results of concentration and reflectance estimations of the painting are shown in Figure 6.10 and Figure 6.11. Comparing estimated concentration maps, both of the methods resulted in rather similar results. In most cases, a reasonable correlation between actual and estimated concentrations was yielded. Particularly, the concentration estimations of primary pigments with more independent spectral shapes; i.e., hansa yellow and quinacridone magenta, were predicted more precisely. The concentration estimations of blue pigments, i.e., cobalt blue and ultramarine blue, contained larger estimation errors because of insufficient spectral sampling required for a perfect differentiation of the blue pigments. When a given camera signal could be reproduced by both of the blue pigments, the algorithm selected either of the blue pigments, which resulted in a random pattern.

Spectra reflectance RMS errors and $\Delta E^*_{94}$ were rather small. Despite ambiguity in concentration estimations of the blue pigments, the spectral estimation errors were quite small for blue areas. The largest errors of the KM-based reconstruction algorithms; i.e., R-LS-KM and R-PCA-KM, corresponded to dark areas and masstones. On the other hand, R-LS and R-PCA methods generated metamer matches for the hansa yellow pigment.
Figure 6.10: Concentration maps corresponding to the R-LS (left column) and the R-PCA (middle column) reconstruction methods. The concentration map on the right corresponds to the concentration estimations using the 2-KM theory and actual primary pigments.
Figure 6.11: RMS errors of spectral reflectances (left), and ΔE°94 (right) for different reflectance reconstruction methods and 2-KM spectral estimations when actual pigment information was used for estimations.
The estimated and actual spectral reflectances for yellow and magenta areas of the painting are shown in Figure 6.12 and Figure 6.13. The R-PCA and R-LS spectral approximations were inaccurate in longer wavelengths and flat reflectance shapes, which resulted in poor estimations for yellow shades. Considering spectral reproduction of the magenta area, the spectral matches imply a similar effect. The spectral mismatches at longer wavelengths did not affect the colorimetric match because of the small spectral sensitivity of the color matching functions. This prediction mismatch was corrected after 2-KM spectral enhancement. However, 2-KM spectral reconstruction might underestimate the pigment concentrations of yellow pigments affecting the quality of the estimated spectral reflectance as explained in Section 5.11.1.1.

![Figure 6.12: Spectral reflectance of the hansa yellow using two spectral reconstruction algorithms. Solid lines represent the spectral reflectance from the LCTF. Circled and dashed lines are spectral estimations before and after KM enhancements respectively.](image-url)
The estimation errors of different spectral reflectance estimation methods for the painting are given in Table 6.1. The 2-KM approximations refer to the spectral reflectances corresponding to the concentration estimation of the low-resolution LCTF capturing system. The low-resolution comparisons are beneficial to separate the estimation errors from the subtractive mixing and the spectral reconstruction steps.

According to the results, the direct PCA and LS-based spectral reconstructions produced smaller $\Delta E^*_{94}$ and spectral reflectance RMS errors. Small average and
maximum $\Delta E^*_{94}$ values for the R-PCA and R-LS methods make them suitable approaches for colorimetric and spectral reconstruction. The estimation errors of KM-based methods were reasonable except for masstones and dark mixtures. The KM-based methods, however, generated more realistic results in most areas of the painting as shown in Figure 6.11. Comparing estimation errors of the 2-KM method and those of the KM-based methods (2-KM estimations after spectral reconstructions) revealed the sensitivity of the KM-based methods to small spectral reflectance deviations for concentration estimation of dark and saturated areas.

A similar procedure can be implemented by using the primary pigments extracted from the unmixing primary pigments presented in Chapter 5. The concentration estimations using the SPICE$^+$ unmixing method are shown in Figure 6.14. The concentration maps using SPICE$^+$ primaries had a reasonable correlation to those of actual pigments and 2-KM predictions. The spectral reproductions for the yellow pigment underwent an analogous effect explained above and in Section 5.11.1.1. Estimation error values in Table 6.2 and Table 6.1 also followed the same general trends. Inefficient spectral estimations of the yellow pigment affected the prediction errors for all the methods even though the R-PCA and R-LS methods maintained their colorimetric accuracy. Note that inaccurate estimations for yellow shades

<table>
<thead>
<tr>
<th>Method</th>
<th>Error Metric</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Maximum</th>
<th>90th Percentile</th>
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</thead>
<tbody>
<tr>
<td>R-PCA</td>
<td>$\Delta E^*_{94}$</td>
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<td>1.4</td>
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<td>0.0452</td>
<td>0.2310</td>
<td>0.0353</td>
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</table>
influenced the direct spectral reflectance methods, since the analogous estimation error was propagated with in the training dataset. Despite large spectral RMS errors for the yellow pigment, other parts of the paintings were estimated reasonably, which verified the validity of using the PI methods for spectral reflectance and concentration map estimations.

Figure 6.14: Concentration maps corresponding to the R-LS (left column) and the R-PCA (middle column) reconstruction methods. The concentration map on the right corresponds to the concentration estimations using the 2-KM theory and using primary pigments from the SPICE+ PI method.
Figure 6.15: RMS errors of spectral reflectances (left), and ΔE*94 (right) for different reflectance reconstruction methods and 2-KM spectral estimations when SPICE® pigment information was used for estimations.
Table 6.2: The total estimation errors of painting 2-1-2 using actual pigments for different spectral reconstruction methods using the SPICE+ primaries.

<table>
<thead>
<tr>
<th>Method</th>
<th>Error Metric</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Maximum</th>
<th>90th Percentile</th>
</tr>
</thead>
<tbody>
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<tr>
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</tr>
<tr>
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</tr>
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</tbody>
</table>

6.4.2 Painting 1-6-3

The painting 1-6-3 with eight primary pigments (yellow ochre, red oxide, ultramarine blue, raw umber, diarylide yellow, chromium oxide green, pyrrole red, cobalt blue) was also examined using similar reconstruction methods. Unlike the previous case, the number of primary pigments is larger than the number of camera channels, which can be considered as underdetermined sets of equations. However, the concentration estimations of the reconstruction methods yielded a reasonable correlation with those of the 2-KM theory (see Figure 6.16 and Figure 6.17). The possibility of reproducing metamer matches might lead to some uncertainty in concentration estimations. Clearly, the probability of metameric reproductions is higher when larger numbers of primary pigments are involved.
Figure 6.16: Concentration maps corresponding to the DualRGB-Concentration (left column) and the Lab-Concentration method (middle column). Concentration maps on the right correspond to the concentration estimations using the 2-KM theory and actual primary pigments.
<table>
<thead>
<tr>
<th>Reproduced Image</th>
<th>Red Oxide</th>
<th>Raw Umber</th>
<th>Payroll Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Reproduced Image]</td>
<td>![Red Oxide]</td>
<td>![Raw Umber]</td>
<td>![Payroll Red]</td>
</tr>
<tr>
<td>![R-LS]</td>
<td>![R-PCA]</td>
<td>![2-KM]</td>
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</table>

Figure 6.16: Continued.
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<th>K/S Curves</th>
<th>ΔE*&lt;sub&gt;94&lt;/sub&gt; (ΔE)</th>
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</table>

**Figure 6.17:** RMS errors of spectral reflectances (left), K/S curves (middle) and ΔE*<sub>94</sub> (right) for three ICC profiles and 2-KM-based spectral estimations when actual pigment information was used for estimations.
The mismatch of the diarylide yellow using the R-PCA algorithm was the only case where the concentration estimation did not correspond to the actual concentrations. Looking at Figure 6.17, the noticeable concentration mismatches belonged to the area with the maximum spectral reflectance estimation errors. The spectral reflectance estimations of the similar area are provided in Figure 6.18. The inaccurate prediction of spectral reconstruction algorithms for long wavelengths was the source of spectral reflectance deviations for the yellow shades. Notice that the R-LS method led to a better estimation of the reflectance in shorter wavelengths, which resulted in a better spectral match in K/S space for the diarylide yellow pigment. Despite large spectral errors, the colorimetric reproductions errors are small because the sensitivity of the capturing system is an appropriate linear combination of the colormatching functions.
Figure 6.18: Spectral reflectance of the diarylide yellow using two spectral reconstruction algorithms. Solid lines represent the spectral reflectance from the LCTF. Circled and dashed lines are spectral estimations before and after KM enhancements respectively.

The estimation error of different methods for the painting is shown in Table 6.3. The maximum prediction errors were relatively large for KM-based algorithms. The R-LS reflectance reconstruction method led to the smallest prediction errors with mean(max) $\Delta E^*_{94}$ of $\sim 0.82$ ($\sim 3.51$), which makes this method the best choice for colorimetric representations.
Table 6.3: Total estimation errors of painting 1-6-3 for reconstruction methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Error Metric</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Maximum</th>
<th>90th Percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-PCA</td>
<td>$\Delta E_{94}$</td>
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<td>1.0</td>
<td>9.2</td>
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<td>R-PCA-KM</td>
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<td>0.0160</td>
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<td>0.0433</td>
</tr>
<tr>
<td>R-LS-KM</td>
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<td>0.9</td>
<td>12.2</td>
<td>1.9</td>
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<tr>
<td></td>
<td>Reflectance RMS</td>
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<td>0.2053</td>
<td>0.0347</td>
</tr>
<tr>
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<td>0.3</td>
<td>19.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Reflectance RMS</td>
<td>0.0055</td>
<td>0.0054</td>
<td>0.2208</td>
<td>0.0126</td>
</tr>
</tbody>
</table>

6.5 High-Resolution Images

An example of high-resolution spectral and concentrations estimations for painting 2-1-2 is demonstrated in this section. For this analysis, the R-LS reconstruction algorithm was selected for preliminary reflectance estimations. The concentration maps derived using 2-KM theory and according to the estimated spectral reflectances. Another spectral reflectance estimations carried our using the calculated concentration maps and 2-KM theory (R-LS-KM). Rendering of R-LS and R-LS-KM spectral images are shown in Figure 6.19. The estimation errors of R-LS-KM algorithm for dark areas and masstones were more noticeable in high-resolution reproductions.

Hight-resolution concentration maps for four pigments are shown in Figure 6.20. Notice that the results of spectral reconstruction are rather similar to those shown in Figure 6.10 but at a higher spatial resolution. Similarly, the estimation uncertainty for the blue shades implied the risk of metamerism in which the camera responses can be reproduced using either of the blue pigments.
Figure 6.19: High-resolution renderings of R-LS (top) and R-LS-KM (bottom) reconstruction algorithms of painting 2-1-2.
Figure 6.20: Concentration maps of painting 2-1-2 calculated from high-resolution six-channel acquisition system based on the R-LS preliminary reconstruction algorithm. Images on the right column correspond to the actual resolution of the areas indicated by the red rectangle in the left column.
Figure 6.21 is a demonstration of the estimated spectral reflectances that correspond to different areas of the painting. Despite of the poor spectral and colorimetric estimations of the KM method for dark areas and masstone, the reflectance estimations were more realistic. The spectral estimation using the R-LS method led to bumpy shapes, which was problematic for reflectances with flat spectral shapes (such as yellow and white shades).

Finally, the processing time comparisons for different steps of concentration and reflectance estimations are summarized in Table 6.4. The largest processing time belonged to the concentration estimations with a non-negative, least-squares algorithm. Notice that spectral estimation steps are rather fast compared to the concentration estimations. The maximum overall time consumption for a full-frame, 48-megapixel image is less than four hours when non-negative least squares algorithm were used for concentration estimations.
Table 6.4: Processing time for concentration and spectral estimation of a 48-megapixel image using a 3.5 GHz Intel Core i7, 32 GB 1600 MHz DDR3 iMac and Matlab 8.1.0.604 (R2013a) 64-bit.

<table>
<thead>
<tr>
<th>Process</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-PCA Spectral Reconstruction</td>
<td>20 Seconds</td>
</tr>
<tr>
<td>R-LS Spectral Reconstruction</td>
<td>7 Seconds</td>
</tr>
<tr>
<td>KM Concentration Estimation (Including Non-negative Least Squares)</td>
<td>220 Minutes</td>
</tr>
<tr>
<td>KM Concentration Estimation (Excluding Non-negative Least Squares)</td>
<td>10 Minutes</td>
</tr>
<tr>
<td>2-KM Reflectance Estimation</td>
<td>40 Seconds</td>
</tr>
</tbody>
</table>

6.6 Conclusions

A practical solution for pigment concentration spectral estimation of six-channel, high-resolution images was provided. The proposed workflow included an intermediate spectral reconstruction step for concentration estimations using two-constant Kubelka-Munk theory (2-KM). Knowing the concentration values, the spectral reflectance of each pixel was calculated using 2-KM theory.

Two types of training-based spectral reflectance reconstruction methods, least-squares and Burns and Berns (1996), were selected for preliminary spectral reconstructions. A uniform distribution of camera responses and pigment concentrations was generated according to camera spectral sensitivities and the primary pigments. The primary pigments were extracted using the pigment identification algorithm explained in Chapter 5. The concentration maps were calculated using the spectral matching method proposed by Walowit, et al., (1988). Eventually, the estimated concentrations were exploited for another estimation to enhance the reconstructed spectral reflectance from analytical methods.

The spectral and concentration estimations applied to two paintings with four and eight primary pigments. Preliminary examinations were carried out on a simulated version of the paintings for pixel-by-pixel error analysis. The estimated concentrations showed a strong correlation with the actual concentrations and led to acceptable average spectral reflectance errors for both paintings. The largest
spectral mismatch belonged to the yellow shads due to insufficient spectral sampling and the risk of negative K/S values in longer wavelengths.

Among spectral reconstruction methods, the direct least-squares method led to the smallest spectral and colorimetric errors. Kubelka-Munk reflectance estimations enhanced the results of most parts of the painting but the dark and saturated areas where the concentration estimations were so sensitive to the precision of spectral reflectance estimations. Both of the direct spectral reconstruction methods generated an excellent colorimetric match even for the areas with rather large reflectance RMS errors.

Finally, the Kubelka-Munk concentration estimation and the least-squares reflectance reconstruction methods were applied to a high-resolution, six-channel image and according preliminary results from the simulated low-resolution image. The high-resolution concentration had a reasonable correlation with those from the simulated images. The processing time for different steps pointed out applicability of the proposed methods on high-resolution image using available personal computers.
CHAPTER 7: CONCLUSIONS AND FUTURE PERSPECTIVES

A novel pipeline for pigment identification of paintings based on spectral images was introduced and evaluated. According to the results, the introduced framework led to a noticeable improvement for pigment identification of the paintings compared to the literature. The implementations and examinations included accurate spectral measurements, a linear subtractive mixing model, pigment identification algorithms and practical use for high-resolution images. Each step was studied and examined in detail.

The pigment identification pipeline started with developing a feasible multispectral imaging system with sufficient measurement precision and accuracy. A liquid crystal tunable filter (LCTF) together with a monochrome CCD camera was selected considering repeatability, cost, measurement time and past research. Capturing geometry, LCTF angular dependency and spectral reflectance reconstruction algorithms were studied more extensively. A new surface correction method based on the Saunderson equation was implemented, evaluated and simplified to address the geometrical dissimilarities between imaging systems and spectrophotometers. The influence of the measurement geometries was assessed by comparing
spectrophotometric and spectroradiometric measurements of a set of validation patches with different surface structures. The results verified the functionality of the Saunderson correction method as a model compensating for appearance changes due to lighting and capturing geometries. Next, the LCTF angular error was examined and reduced using a set of matte solid color sheets and a spatial wavelength-based Berns-Petersen correction method. The LCTF angular shift effect was evaluated by a set of standard color patches placed in different positions within scene. The introduced angular correction algorithm reduced the average CIEDE2000 values from ~1.8 to ~0.5 for a standard color target according to its location in the scene. Finally, spectral reflectances were estimated from dark corrected, linearized camera signals after LCTF angular shift and geometry corrections. The spectral reconstruction method was also based on the Bern-Petersen correction formulation considering the characteristics of the LCTF system. The mean (max) CIEDE2000 of ~0.44 (~1.65) and spectral reflectance RMS of ~0.7% (2.5%) for a validation target showed a reasonable spectral accuracy and precision for pigment identification. Eventually, the acquired spectral data from the spectral imaging system were utilized for pigment information in the next step.

The implementation of a linear subtractive mixing model was an exclusive and vital element of this dissertation. A new modification of Kubelka-Munk (KM) theory was derived to enable the use of linear spectral unmixing algorithms for pigment identification. Next, the overall performance of KM theory and the linearized modification were evaluated over a variety of pigment types and concentrations. An analysis of spectral RMS errors pointed out that the general form of KM theory is not effective for dark masstimes. Additionally, the new modification generated accurate spectral predictions only for light and pale shades but reasonable concentration estimations for other shades. The results enabled the usage of linear unmixing algorithms for a preliminary estimation of primary pigment using light and pale shades where the modified KM theory is accurate and provides linearity. Extracted primary information was used for concentration estimation of light and darker areas. Finally, the coefficients of each primary pigment were derived using original
KM theory for opaque layers according to the estimated concentrations for light and medium shades.

Three spectral unmixing algorithms were selected and modified to extract the pigment information from the spectral images using the defined subtractive mixing model. A preliminary preparation step was applied to the spectral data to extract a uniform and effective distribution of spectral pixels for further analyses. Final sets of primary pigments were compared to a pre-existing database of actual pigments for verification purposes. The efficiency of pigment selection and pigment identification algorithms was evaluated using 23 validation paintings with known primary pigments. The pigment comparison was able to predict the exact pigments with a $\sim 76\%$ correct prediction rate. The quality of the pigment identification relied on the image content and the number and the dependency of constituent primary pigments. The concentration and spectral RMS images, as metrics of overall performance of pigment identification, revealed a reasonable correlation for most of the paintings.

The visualization of the concentration and spectral data for high-resolution images was the last piece to make the proposed workflow applicable for museums. A combination of direct and KM-based algorithms was used for spectral and pigment concentration estimations. The spectral reconstruction methods were evaluated and applied to a simulated version of two test paintings for spectral estimation. According to the results, direct spectral reconstruction methods generated smaller RMS and colorimetric errors for the entire painting. Finally, the results were expanded for estimating the concentration maps of a high-resolution six-channel image of the test painting with four primary pigments. The processing time of different steps revealed the applicability of the proposed workflow for high-resolution imagery.
7.1 Future Perspectives

The proposed workflow for spectral image-based pigment identification led to a new and novel alternative for analysis of paintings in museums. The results of this research can be refined and expanded from different aspects. Below is a list of suggestions for future work:

- The LCTF-based spectral imaging system introduced in this research provided accurate spectral images compared to other techniques in the literature. However, the imaging system still can be enhanced from different aspects. The camera sensor, optical system and illumination facilities can be the subject of further enhancements. Replacing the current low-resolution CCD camera with a high-resolution sensor will influence the pigment identification performance by providing more precise spectral information per pixel. Clearly, a high-resolution camera sensor demands extra research on developing a high-performance optical path with smaller optical aberrations of the lens system and the LCTF. The repeatability and noise level of the capturing system, particularly in UV and IR, were other sources of error in spectral measurement. Evaluating and expanding the effective wavelength range as well as a practical illumination system can lead to considerable improvement in pigment identification.

- Despite the conventional use of KM theory for color matching of subtractive mixtures, its application for image-base analysis requires new evaluations. Spectral predictions of masstones and saturated shades, accurate estimation of the Saunderson coefficients, singularity of the KM coefficient matrix, non-negative and perceptual-based spectral matching creates a multivariable problem that can be improved with further independent research. The scattering behavior of the artists' pigments and its correlation with KM coefficients is another field of research that requires more fundamental
studies of the material properties. The results will be helpful for characterizing masstones and dark shades in the paintings.

- The proposed modification for KM theory can be the subject of further analyses for spectral-based image processes in a subtractive mixing space. The linearity of the equations enable the implementation of different image processing algorithms, such as segmentation and clustering, but in a linear mixing space.

- The performance of the pigment identification algorithms varies depending on the selected spectral unmixing algorithm. The introduced unmixing algorithms can be replaced by variety of available spectral unmixing methods for pigment identification purposes. Spatial-based algorithms, such as Automatic Morphological End-member Extraction (AMEE) and Bayesian-based unmixing techniques, are potential solutions that reduce the uncertainty of the predictions. Defining an appropriate distance function that includes perceptual and spectral error is an important part of the pigment identification workflow that should be examined in more depth.

- Noise characterization and developing more sophisticated dimensionality reduction techniques in the subtractive mixing space can also be subjects of further research. The results are specifically applicable for employing existing dimensionality determination algorithms in remote sensing.

- The database comparison is another topic for more evaluations. Combining future detection and pattern recognition algorithms can enhance the comparison results. The pre-existing database can be the subject of preliminary examinations so that the extracted signatures reveal material characteristics instead of pigment names.
• Implementation of direct spectral estimation workflow and its applicability for concentration estimation purposes require further studies and evaluations. Evaluations and applications of a variety of available spectral reconstruction techniques applicable for high-resolution images and concentration estimation can be pursued in independent research.

• Eventually, the pigment identification workflow can be implemented within the newly developed spectral-based ICC profiles for spectral color managements, manipulations and visualizations. Ultimately, It provides a unique platform for integrating a variety of spectral-based procedures, such as pigment identification, into a user-friendly and accessible package.

7.2 Publications

This research resulted in a number of journal and conference publications:


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APPENDIX A

This appendix includes mathematical steps for deriving Eq. 3.4 from Eq. 3.3:

Eq. 3.3 can be rewritten as follows:

\[ R_{m,e} = \frac{(1 - k_1)(1 - k_2)R_m - (1 - k_1)(1 - k_2)k'_{ins}k'_1}{(1 - k'_1)(1 - k'_2) - k'_{ins}k'_1k'_2 + k'_{ins}k'_1k'_2 + R_m(k_2 - k'_2)} + k_{ins}k_1 \]  

Eq. A.1

or

\[ R_{m,e} = \frac{R_m + \frac{DC + E}{DB - A}}{B} \frac{1}{R_m + \frac{C}{DB - A}} \]  

Eq. A.2

where \( A, B, C, D, E \) are defined as:

\[ A = (1 - k_1)(1 - k_2) \]  

Eq. A.3

\[ B = (k_2 - k'_2) \]  

Eq. A.4

\[ C = (1 - k'_1)(1 - k'_2) - k'_{ins}k'_1k'_2 + k'_{ins}k'_1k_2 \]  

Eq. A.5
\[ D = k_{\text{ins}}k_1 \]  
\[ E = (1 - k_1)(1 - k_2)k'_{\text{ins}}k'_1 \]

By defining further auxiliary variables, the following equation is derived:

\[ R'_m = \frac{R_m + \alpha}{\beta R_m + \gamma} \]

where \( \alpha = \frac{D_{C+E}}{D_{B-A}}, \beta = \frac{B}{D_{B-A}}, \gamma = \frac{C}{D_{B-A}}. \)
APPENDIX B

This appendix shows the mathematical steps for deriving Eq. 3.5:

By letting \(k_2\) equal to \(k'_2\) in Eq. 3.3:

\[
R_{m,c} = \frac{(1 - k_1)(1 - k_2)R_m - (1 - k_1)(1 - k_2)k'_1 k_1' + k'_1 k'_2 + R_m (k_2 - k'_2)}{(1 - k'_1)(1 - k'_2)} + k_{ins} k_1
\]

Eq. B.1

Then

\[
R_{m,c} = \frac{(1 - k_1)R_m - (1 - k_1)k'_1 k_1'}{(1 - k'_1)} + k_{ins} k_1
\]

Eq. B.2

By reforming this equation based on variable \(R_m\), the following equation is obtained:

\[
R_{m,c} = \left(\frac{1 - k_1}{1 - k'_1}\right) R_m + k_{ins} k_1 - \left(\frac{1 - k_1}{1 - k'_1}\right) k'_1 k_1'
\]

Eq. B.3

which is similar to the equation below:

\[
R_{m,c} = \mu R_m + \rho
\]

Eq. B.4

where \(\mu = \left(\frac{1 - k_1}{1 - k'_1}\right)\) and \(\rho = + k_{ins} k_1 - \left(\frac{1 - k_1}{1 - k'_1}\right) k'_1 k_1'.\)
APPENDIX C

Different steps of the proposed spectral characterization procedure are compared in this appendix. A rendition of the ColorChecker Passport and the MCLS color target are shown in Figure C.1 and Figure C.2. The influence of each step for training and validation color targets is shown in Figure C.3 to Figure C.6. Figure C.3 and Figure C.4 illustrate the actual and estimated color CIELAB color space. The linearity of the acquisition system is evaluated for each step by plotting the CIE-Y values of the gray patches of the Classic ColorChecker Passport in right column of Figure C.3. The spectral reconstruction performances for two color targets are shown in Figure C.5 and Figure C.6. The residual spectral reflectances are shown in Figure C.7 and Figure C.8.
Figure C.1: A render of ColorChecker Passport for four steps of characterization process.
Figure C.2: A render of MCSL color target for four steps of characterization process.
Figure C.3: Plots of CIEAB (left), CIELC (middle) the CIEY values of the gray patches (right) of the Classic ColorChecker calculated form actual (measured by spectroradiometer) and estimated reflectance in each step of characterization. In CIELAB plots, filled circles represent estimated values of the custom color chart. The line connected to each circle shows the location of the actual value.
Figure C.4: Plots of CIELAB $a^*\cdot b^*$ (left), CIELAB $L^*\cdot C^*$ (right) to the MCSL color target calculated from actual (measured by spectroradiometer) and estimated reflectance in each step of characterization. The filled circles represent estimated values of the custom color chart. The line connected to each circle shows the location of the actual value.
Figure C.5: Actual (solid black) and estimated (dashed red) reflectance factors of the ColorChecker Passport patches for different steps of characterization. For each patch, the number at top-left corner indicates CIEDE2000 value between actual and predicted curves. The color of each sample is divided into two upper and lower triangles. The upper and lower triangles are rendered corresponded to the predicted and actual reflectance factors respectively.
Figure C.6: Actual (solid black) and estimated (dashed red) reflectance factors of the MCSL color target for different steps of characterization. For each patch, the number at top-left corner indicates CIEDE2000 value between actual and predicted curves. The color of each sample is divided into two upper and lower triangles. The upper and lower triangles are rendered corresponded to the predicted and actual reflectance factors respectively.
Figure C.7: The residual reflectance factors of the Classic ColorChecker passport for different steps of characterization.

Figure C.8: The residual reflectance factors of the MCSL color target for different steps of characterization.
APPENDIX D

The spectral reproduction performances of three methods explained in Section 3.2.2.3 are provided in this appendix. Figure D.1 is a plot showing estimated and actual spectral reflectance factors for each method. The figure includes the CIEDE2000 along with a color representation of the patches for actual and estimated spectra. The spectral residual error of the spectral reconstruction is shown Figure D.2.
Figure D.1: Actual (solid black) and estimated (dashed red) reflectance factors of the glossy patches of custom color target for different characterization methods explained in Section 3.2.2.3. For each patch, the number at top-left corner indicates CIEDE2000 value between actual and predicted curves. The color of each sample is divided into two upper and lower triangles. The upper and lower triangles are rendered corresponded to the predicted and actual reflectance factors respectively.
Figure D.2: The residual reflectance factors of 50 glossy samples of the costume color target for different characterization methods.
APPENDIX E

The pigment identification algorithm was applied to 23 paintings with known constituent pigments. Two major categories of pigments were selected: old master and moderns. Each category contains several paintings with different number of primary pigments indicated in Table E.1 and Table E.2. The colorimetric images of the paintings are shown in Figure E.2 and Figure E.1.

Table E.1: List of the old master pigment paintings

<table>
<thead>
<tr>
<th>Index</th>
<th>Constituent Pigments (Number of pigments)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1-1</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue (3)</td>
</tr>
<tr>
<td>1-1-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue (3)</td>
</tr>
<tr>
<td>1-2-1</td>
<td>Yellow Ochre, Red Oxide, Cobalt Blue, Raw Umber (4)</td>
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<tr>
<td>1-2-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber (4)</td>
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<td>1-3-1</td>
<td>Diarylide Yellow, Red Oxide, Ultramarine Blue, Raw Umber, Black (5)</td>
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<td>1-3-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Black (5)</td>
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<td>1-4-1</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green (6)</td>
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<tr>
<td>1-4-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green (6)</td>
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<td>1-5-1</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red (7)</td>
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<td>1-5-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red (7)</td>
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<td>1-5-3</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red (7)</td>
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<tr>
<td>1-6-1</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red, Cobalt Blue (8)</td>
</tr>
<tr>
<td>1-6-2</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red, Cobalt Blue (8)</td>
</tr>
<tr>
<td>1-6-3</td>
<td>Yellow Ochre, Red Oxide, Ultramarine Blue, Raw Umber, Diarylide Yellow, Chromium Oxide Green, Pyrrole Red, Cobalt Blue (8)</td>
</tr>
</tbody>
</table>

Table E.2: List of the modern pigment paintings
<table>
<thead>
<tr>
<th>Code</th>
<th>Constituent Pigments (Number of pigments)</th>
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<tr>
<td>2-1-1</td>
<td>Cobalt Blue, Ultramarine Blue, Quinacridone Magenta, Hansa Yellow (4)</td>
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<tr>
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<td>Cobalt Blue, Ultramarine Blue, Quinacridone Magenta, Hansa Yellow (4)</td>
</tr>
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<td>Cobalt Blue, Ultramarine Blue, Quinacridone Magenta, Hansa Yellow, Phthalo Blue, Pyrrole Red (6)</td>
</tr>
<tr>
<td>2-2-2</td>
<td>Cobalt Blue, Ultramarine Blue, Quinacridone Magenta, Hansa Yellow, Phthalo Blue, Pyrrole Red (6)</td>
</tr>
<tr>
<td>2-3-1</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3)</td>
</tr>
<tr>
<td>2-3-2</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow (3)</td>
</tr>
<tr>
<td>2-7-1</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow, Pyrrole Red, Phthalo Green, Carbon Black (6)</td>
</tr>
<tr>
<td>2-8-1</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow, Pyrrole Red, Phthalo Green, Carbon Black, Diarylide Yellow (7)</td>
</tr>
<tr>
<td>2-8-2</td>
<td>Phthalo Blue, Quinacridone Magenta, Hansa Yellow, Pyrrole Red, Phthalo Green, Carbon Black, Diarylide Yellow (7)</td>
</tr>
</tbody>
</table>
Figure E.1: Colorimetric images of the validation paintings comprised of old master pigments. The numbers are corresponded to the paintings’ code in Table E.1.
Figure E.2: Colorimetric images of the validation paintings comprised of modern pigments. The numbers are corresponded to the paintings’ code in Table E.2.
APPENDIX F

CIEDE2000, spectral reflectance RMS and concentration errors of the predictions of 28 pigment ramps corresponding to Section 4.1.2.1 are shown in Figure F.1 to Figure F.6. The estimation errors are associated with the test and training dataset with and without masstines. The results are expressed in linear and log scales for better comparisons.
Figure F.1: The mean CIEDE2000 of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
Figure F.2: The log scale mean CIEDE2000 of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
Figure F.3: The mean spectral reflectance RMS errors of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
Figure F.4: The log scale mean spectral reflectance RMS errors of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
Figure F.5: The mean concentration RMS errors of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
Figure F.6: The log scale mean concentration RMS errors of actual and estimated K/S for 28 pigments with (bottom) and without (top) masstones in the training dataset. The vertical axis indicates the training dataset used for estimations.
APPENDIX G

CIEDE2000, spectral reflectance RMS and concentration errors of the predictions of 28 pigment ramps corresponding to Section 4.1.2.1. The estimation errors are associated with the test and training dataset when masstones are removed from the evaluation dataset. Each figure contains the estimation errors for the training set with and without masstones.
Figure G.1: The mean CIEDE2000 of actual and estimated K/S for 28 pigments when masstones are removed from validation set. The plot illustrates the prediction with training set with (bottom) and without (top) masstones. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error.
Figure G.2: The mean spectral reflectance RMS error of actual and estimated K/S for 28 pigments when masstones are removed from validation set. The plot illustrates the prediction with training set with (bottom) and without (top) masstones. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error.
Figure G.3: The mean concentration RMS error of actual and estimated K/S for 28 pigments when masstones are removed from validation set. The plot illustrates the prediction with training set with (bottom) and without (top) masstones. The vertical axis indicates the training dataset used for estimations. The filled dots show the median of the error.
APPENDIX H

This appendix contains average CIEDE2000, concentration RMS, and spectral reflectance RMS errors for combinations of three chromatic pigments for a variety of training and validation datasets corresponding to Section 4.1.2.2.

Figure H.1: The mean CIEDE2000 of actual and estimated K/S for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refer to the total number of samples in each dataset. The filled circles represent median of the error.
Figure H.2: The mean spectral reflectance RMS error of actual and estimated K/S for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training set were calculated for six testing sets. The numbers in parentheses refer to the total number of samples in each dataset. The filled circles represent median of the error.

Figure H.3: The mean concentration RMS of actual and estimated K/S for different testing data and different tint ladders as training datasets. The vertical axis indicates the training dataset used for estimations. The RMS of errors of each training collection was calculated for six testing sets. The numbers in parentheses refer to the total number of samples in each dataset. The filled circles represent median of the error.
APPENDIX I

The final results of pigment identification for the validation paintings are shown in this Appendix. Colorimetric images of the paintings, extracted endmembers using four unmixing methods, error images and concentration maps are illustrated separately. The paintings were created using the pigments shown in Figure I.1.

Figure I.1: Primary pigments used in creating the validation paintings: titanium white, carbon black, phthalo green, phthalo blue, cobalt blue, ultramarine blue, hansa yellow, quinacridone magenta, pyrrole red, red oxide, yellow ochre, diarylide yellow, chromium oxide green, ultramarine blue, raw umber.
Painting 1-1-1

Figure I.2: Colorimetric image of the painting 1-1-1

Figure I.3: Final endmembers extracted in each iteration using SGA⁺ and SGA.
Figure 1.4: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1.5: Concentration maps corresponding to SPICE (left) and SPICE\+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 1-1-2

Figure I.6: Colorimetric image of the painting

Figure I.7: Final endmembers extracted in each iteration using SGA* and SGA.
Figure I.8: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.9: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 1-2-1

Figure I.10: Colorimetric image of the painting

Figure I.11: Final endmembers extracted in each iteration using SGA\(^+\) and SGA.
Figure 1.12: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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Figure I.I3: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and the actual primary pigments.
Painting 1-2-2

Figure I.14: Colorimetric image of the painting

Figure I.15: Final endmembers extracted in each iteration using SGA* and SGA.
Figure 1.16: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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<th>Yellow Ochre</th>
<th>Raw Umber</th>
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Figure L17: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 1-3-1

Figure 1.18: Colorimetric image of the painting

Figure 1.19: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.20: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1.21: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 1-3-2

Figure I.22: Colorimetric image of the painting

Figure I.23: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure 1.24: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1.25: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 1-4-1

Figure 1.26: Colorimetric image of the painting

Figure 1.27: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure 1.28: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.29: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
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Figure I.29: Continued.
Painting 1-4-2

Figure I.30: Colorimetric image of the painting

Figure I.31: Final endmembers extracted in each iteration using SGA* and SGA.
Figure I.32: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.33: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
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**Figure I.33:** Continued.
Painting 1-5-1

Figure I.34: Colorimetric image of the painting

Figure I.35: Final endmembers extracted in each iteration using SGA⁺ and SGA.
Figure I.36: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
<table>
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<tr>
<th>Reproduced Image</th>
<th>Chromium Oxide Green</th>
<th>Red Oxide</th>
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<th>Pyrrole Red</th>
<th>Yellow Ochre</th>
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</table>

Figure 1.37: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.37: Continued.
Painting 1-5-2

Figure I.38: Colorimetric image of the painting

Figure I.39: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.40: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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<th>Yellow Ochre</th>
<th>Pyrrole Red</th>
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</table>

Figure I.41: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.41: Continued.
Painting 1-5-3

Figure I.42: Colorimetric image of the painting

Figure I.43: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.44: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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Figure I.45: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
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Figure I.45: Continued.
Painting 1-6-1

Figure 1.46: Colorimetric image of the painting

Figure 1.47: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure 1.48: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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<td>Cobalt Blue</td>
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</table>

**Figure I.49:** Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.49: Continued.
Painting 1-6-2

Figure I.50: Colorimetric image of the painting

![Colorimetric image of the painting](image)

Figure I.51: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure 1.52: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.53: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.53: Continued.
Painting 1-6-3

Figure I.54: Colorimetric image of the painting

Figure I.55: Final endmembers extracted in each iteration using SGA* and SGA.
Figure 1.56: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
<table>
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Figure I.57: Concentration maps corresponding to SPICE (left) and SPICE⁺ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
<table>
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</table>

*Figure I.57: Continued.*
Painting 2-1-1

Figure I.58: Colorimetric image of the painting

Figure I.59: Final endmembers extracted in each iteration using SGA⁺ and SGA.
Figure I.60: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1G1: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 2-1-2

Figure I.62: Colorimetric image of the painting

Figure I.63: Final endmembers extracted in each iteration using SGA* and SGA.
Figure I.64: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1.65: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 2-2-1

Figure I.66: Colorimetric image of the painting

Figure I.67: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.68: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure 1.69: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
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Figure I.69: Continued.
Painting 2-2-2

Figure I.70: Colorimetric image of the painting

Figure I.71: Final endmembers extracted in each iteration using SGA and SGA+.
Figure 1.72: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.73: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.73: Continued.
Painting 2-3-1

Figure 1.74: Colorimetric image of the painting

Figure 1.75: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.76: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.77: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 2-3-2

Figure 1.78: Colorimetric image of the painting

Figure 1.79: Final endmembers extracted in each iteration using SGA and SGA.
Figure I.80: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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Figure 1.81: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Painting 2-7-2

Figure 1.82: Colorimetric image of the painting

Figure 1.83: Final endmembers extracted in each iteration using SGA⁺ and SGA.
Figure I.84: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.85: Concentration maps corresponding to SPICE (left) and SPICE’ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
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<table>
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**Figure I.85: Continued.**
Painting 2-8-1

Figure L86: Colorimetric image of the painting

Figure L87: Final endmembers extracted in each iteration using SGA+ and SGA.
Figure I.88: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
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<td><img src="image2.jpg" alt="Image" /></td>
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<td><img src="image8.jpg" alt="Image" /></td>
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<td><img src="image19.jpg" alt="Image" /></td>
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</tr>
</tbody>
</table>

Figure 1.89: Concentration maps corresponding to SPICE (left) and SPICE* method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Reproduced Image

Diarylute Yellow

Hansa Yellow

Quinacridone Magenta

Figure I.89: Continued.
Painting 2-8-2

Figure I.90: Colorimetric image of the painting
Figure I.91: Final endmembers extracted in each iteration using SGA+ and SGA.

Figure I.92: RMS errors of spectral reflectances (left) and K/S curves (right) for different pigment identification methods.
Figure I.93: Concentration maps corresponding to SPICE (left) and SPICE+ method (middle). The concentration map on the right is corresponded to the concentration estimations using 2-KM theory and actual primary pigments.
Figure I.93: Continued.
APPENDIX J

The summary of pigment identification average RMS and 90th percentile error for the validation paintings for four sets of primary pigments are shown Tables J.1 to J-3. In these tables actual and selected columns are referred to the actual and selected pigment set with the smallest 90th percentile of spectral reflectance RMS correspondingly.
### Table J.1: A summary of 90th percentile and average of different error metrics for old master validation paintings.

<table>
<thead>
<tr>
<th>Painting</th>
<th>Error Metric</th>
<th>90th Percentile</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SPICE</td>
<td>SPICE+</td>
</tr>
<tr>
<td>1-1-1</td>
<td>( \Delta E^* )</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0116</td>
<td>0.0089</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0173</td>
<td>0.0174</td>
</tr>
<tr>
<td>1-1-2</td>
<td>( \Delta E^* )</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.012</td>
<td>0.0109</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0468</td>
<td>0.0486</td>
</tr>
<tr>
<td>1-2-1</td>
<td>( \Delta E^* )</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0063</td>
<td>0.0076</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.1306</td>
<td>0.1013</td>
</tr>
<tr>
<td>1-2-2</td>
<td>( \Delta E^* )</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0069</td>
<td>0.0066</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0642</td>
<td>0.0694</td>
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<tr>
<td>1-3-1</td>
<td>( \Delta E^* )</td>
<td>0.4</td>
<td>0.3</td>
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<td>Reflectance</td>
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<td>0.0017</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.111</td>
<td>0.0863</td>
</tr>
<tr>
<td>1-3-2</td>
<td>( \Delta E^* )</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0042</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0622</td>
<td>0.0509</td>
</tr>
<tr>
<td>1-4-1</td>
<td>( \Delta E^* )</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0039</td>
<td>0.0028</td>
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<tr>
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<td>K/S</td>
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<td>0.08</td>
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<tr>
<td>1-4-2</td>
<td>( \Delta E^* )</td>
<td>0.4</td>
<td>0.4</td>
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<td>Reflectance</td>
<td>0.0082</td>
<td>0.0081</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.059</td>
<td>0.0502</td>
</tr>
<tr>
<td>1-5-1</td>
<td>( \Delta E^* )</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0034</td>
<td>0.0027</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0487</td>
<td>0.0399</td>
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<tr>
<td>1-5-2</td>
<td>( \Delta E^* )</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0084</td>
<td>0.0054</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.045</td>
<td>0.0406</td>
</tr>
<tr>
<td>1-5-3</td>
<td>( \Delta E^* )</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td></td>
<td>Reflectance</td>
<td>0.0075</td>
<td>0.0057</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.0285</td>
<td>0.0264</td>
</tr>
<tr>
<td>1-6-1</td>
<td>( \Delta E^* )</td>
<td>0.2</td>
<td>0.1</td>
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<tr>
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<td>Reflectance</td>
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<td>0.004</td>
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<td>K/S</td>
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<td>0.0981</td>
</tr>
<tr>
<td>1-6-2</td>
<td>( \Delta E^* )</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0067</td>
<td>0.0051</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.0296</td>
<td>0.0332</td>
</tr>
<tr>
<td>1-6-3</td>
<td>( \Delta E^* )</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0046</td>
<td>0.0055</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.0459</td>
<td>0.0436</td>
</tr>
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<td>Painting</td>
<td>Error Metric</td>
<td>90th Percentile</td>
<td>Average</td>
</tr>
<tr>
<td>----------</td>
<td>--------------</td>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SPICE SPICE+ Selected Actual</td>
<td>SPICE SPICE+ Selected Actual</td>
</tr>
<tr>
<td>2-1-1</td>
<td>ΔE*94</td>
<td>0.4 0.3 0.2 0.5</td>
<td>0.7 0.5 0.4 0.8</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0123 0.0155 0.011 0.0282</td>
<td>0.0208 0.0306 0.0188 0.0792</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.1013 0.0867 0.1003 0.1329</td>
<td>0.1971 0.1843 0.2576 0.3118</td>
</tr>
<tr>
<td>2-1-2</td>
<td>ΔE*94</td>
<td>0.6 0.8 0.5 0.8</td>
<td>1.2 1.4 0.8 1.4</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0219 0.0296 0.0132 0.0223</td>
<td>0.0438 0.1035 0.0203 0.0353</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.222 0.2127 0.1327 0.1805</td>
<td>0.3261 0.342 0.263 0.4238</td>
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<tr>
<td>2-2-1</td>
<td>ΔE*94</td>
<td>0.6 0.4 0.8 0.8</td>
<td>1.4 0.8 1.7 1.8</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0265 0.0138 0.0297 0.0192</td>
<td>0.07 0.0254 0.0697 0.0373</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.1099 0.171 0.3621 0.2359</td>
<td>0.241 0.3556 0.4215 0.4796</td>
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<tr>
<td>2-2-2</td>
<td>ΔE*94</td>
<td>0.5 0.5 0.6 0.5</td>
<td>1.2 1.1 1.2 1.3</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0174 0.0159 0.013 0.0116</td>
<td>0.0501 0.0448 0.0247 0.0242</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.1484 0.1739 0.3001 0.2602</td>
<td>0.3447 0.465 0.4439 0.494</td>
</tr>
<tr>
<td>2-3-1</td>
<td>ΔE*94</td>
<td>4.8 6.3 3.6 3.6</td>
<td>10.2 14.6 7.3 7.3</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0657 0.0633 0.0381 0.0381</td>
<td>0.1476 0.162 0.0857 0.0857</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.3543 0.4509 0.5602 0.5602</td>
<td>0.7639 0.9457 0.7033 0.7033</td>
</tr>
<tr>
<td>2-3-2</td>
<td>ΔE*94</td>
<td>2.6 2.3 3.4 3.4</td>
<td>6.4 4.7 7.1 7.1</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0312 0.0305 0.025 0.025</td>
<td>0.0691 0.0945 0.0509 0.0509</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.2152 0.1962 0.9106 0.9106</td>
<td>0.5613 0.5451 0.505 0.505</td>
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<tr>
<td>2-7-2</td>
<td>ΔE*94</td>
<td>1.7 1.7 1.1 1.5</td>
<td>1.3 1 2 1.7</td>
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<tr>
<td></td>
<td>Reflectance</td>
<td>0.0475 0.0423 0.0354 0.0355</td>
<td>0.0679 0.0635 0.0425 0.0283</td>
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<tr>
<td></td>
<td>K/S</td>
<td>0.3779 0.4051 0.4056 0.4076</td>
<td>0.5627 0.6968 0.997 0.679</td>
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<tr>
<td>2-8-1</td>
<td>ΔE*94</td>
<td>1.4 2.4 1.1 3.4</td>
<td>2.7 2.2 1.3 2.5</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0542 0.0368 0.046 0.0499</td>
<td>0.1134 0.0915 0.0581 0.0662</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.2639 2.4614 0.5647 11.9555</td>
<td>0.384 1.2526 0.5656 0.6179</td>
</tr>
<tr>
<td>2-8-2</td>
<td>ΔE*94</td>
<td>0.6 0.5 0.9 0.8</td>
<td>1.4 1.1 1 1.2</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>0.0225 0.0194 0.0198 0.0136</td>
<td>0.0805 0.0812 0.0402 0.0348</td>
</tr>
<tr>
<td></td>
<td>K/S</td>
<td>0.195 0.2274 0.6756 0.3305</td>
<td>0.4474 0.4464 0.594 0.5275</td>
</tr>
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</table>
Table J.3: A summary of 90th percentile and average of different error metrics for old master, modern and all of the validation paintings.

<table>
<thead>
<tr>
<th>Metric</th>
<th>90th Percentile</th>
<th></th>
<th>Average</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Modern Old Master</td>
<td>Total Modern Paintings Old Master</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ΔE*94</strong></td>
<td>SPICE 1.7 3.0 0.9</td>
<td>0.7 1.3</td>
<td>0.4</td>
<td>SPICE+ 1.6 3.0 0.7</td>
</tr>
<tr>
<td>Selected</td>
<td>1.4 2.5 0.7</td>
<td>0.7 1.2</td>
<td>0.3</td>
<td>Actual 1.6 2.8 0.7</td>
</tr>
<tr>
<td><strong>Reflectance RMS</strong></td>
<td>SPICE 0.0361 0.0737 0.0119</td>
<td>0.0151 0.0283</td>
<td>0.0065</td>
<td>SPICE+ 0.0363 0.0774 0.0098</td>
</tr>
<tr>
<td>Selected</td>
<td>0.0259 0.0457 0.0132</td>
<td>0.0123 0.0204</td>
<td>0.0071</td>
<td>Actual 0.0271 0.0491 0.0130</td>
</tr>
<tr>
<td><strong>K/S RMS</strong></td>
<td>SPICE 0.2653 0.4254 0.1624</td>
<td>0.1125 0.1835</td>
<td>0.0669</td>
<td>SPICE+ 0.3054 0.5815 0.1279</td>
</tr>
<tr>
<td>Selected</td>
<td>0.3074 0.5279 0.1656</td>
<td>0.2183 0.4278</td>
<td>0.0837</td>
<td>Actual 0.3103 0.5219 0.1743</td>
</tr>
</tbody>
</table>
APPENDIX K

This Appendix includes spectral reflectance of 28 Golden matte artist acrylic disperse paints, available in Okumura’s pigment database (Okumura, 2005). Each ramp of the pigments is shown in an independent plot (Figure K.1). The database is comprised of several concentrations of the pigments with titanium white drawn down on black and white substrate to obtain opaque paint layers. Several drawdowns were made for each pigment with respect to the strength of the colorant. The spectral reflectance of the opaque layers was measured by a GretagMacbeth Color Eye XTH spectrophotometer with integrating sphere and specular component included (di:8°). More information of the pigments is provided in Table K.1.
### Table K.1: List of GOLDEN paint names, C.I. Name and pigment names.

<table>
<thead>
<tr>
<th>Paint Name</th>
<th>C.I. Name</th>
<th>Pigment Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanent Green Light</td>
<td>PY 3 / PG 7</td>
<td>Acrylate Yellow Chlorinated Copper Phthalocyanine</td>
</tr>
<tr>
<td>Chromium Oxide Green</td>
<td>PG 17</td>
<td>Alumhydroxide Chromium Sesquioxide</td>
</tr>
<tr>
<td>Green Gold</td>
<td>PY 150 / PG 36 / PY 3</td>
<td>Nickel Complex Azo Brominated &amp; Chlorinated - Copper Phthalocyanine</td>
</tr>
<tr>
<td>Yellow Oxide</td>
<td>PY 43</td>
<td>Natural Hydrated Iron Oxide</td>
</tr>
<tr>
<td>Raw Sienna</td>
<td>PB 7</td>
<td>Natural Iron Oxide</td>
</tr>
<tr>
<td>Burnt Sienna</td>
<td>PB 7</td>
<td>Calcined Natural Iron Oxide</td>
</tr>
<tr>
<td>Red Oxide</td>
<td>PR 101</td>
<td>Synthetic Red Iron Oxide</td>
</tr>
<tr>
<td>Burnt Umber</td>
<td>PB 7</td>
<td>Natural Iron Oxide containing Manganese</td>
</tr>
<tr>
<td>Raw Umber</td>
<td>PB 7</td>
<td>Calcined Natural Iron Oxide containing Manganese</td>
</tr>
<tr>
<td>Paynes Gray</td>
<td>PB 29 / PBk 7</td>
<td>Ultramarine Blue Carbon Black</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>PBk 7</td>
<td>Nearly Pure Amorphous Carbon</td>
</tr>
<tr>
<td>Titan Buff</td>
<td>PW 6</td>
<td>Titanium Dioxide Rutile</td>
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<td>Zinc White</td>
<td>PW 4</td>
<td>Zinc Oxide</td>
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<td>Titanium White</td>
<td>PW 6</td>
<td>Titanium Dioxide Rutile</td>
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<td>Hanko Yellow Opaque</td>
<td>PY 74</td>
<td>Acrylate Yellow SOX</td>
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<td>Diazoide Yellow</td>
<td>PY 83</td>
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<td>Pyrrole Red</td>
<td>PR 254</td>
<td>Diglycolglycol</td>
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<tr>
<td>Naphthol Red Medium</td>
<td>PR 5</td>
<td>Naphthol ITR</td>
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<tr>
<td>Quinacridone Crimson</td>
<td>PR 206 / PR 202</td>
<td>Quinacridone</td>
</tr>
<tr>
<td>Quinacridone Magenta</td>
<td>PR 122</td>
<td>Quinacridone</td>
</tr>
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<td>Dioxazine Purple</td>
<td>PV 23</td>
<td>Carbonate Dioxazine</td>
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<tr>
<td>Alizarin Redlake</td>
<td>PB 60</td>
<td>Indanthrone Blue</td>
</tr>
<tr>
<td>Ultramarine Blue</td>
<td>PB 29</td>
<td>Polyoxodile of Sodium-Alumina-Silicate</td>
</tr>
<tr>
<td>Cobalt Blue</td>
<td>PB 26</td>
<td>Oxides of Cobalt and Aluminum</td>
</tr>
<tr>
<td>Cerussina Blue, Chromium</td>
<td>PB 36.1</td>
<td>Oxides of Cobalt and Chromium</td>
</tr>
<tr>
<td>Phthalocyan Blue (Green Shade)</td>
<td>PB 15-4</td>
<td>Copper Phthalocyanise</td>
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<tr>
<td>Phthalocyan Green (Blue Shade)</td>
<td>PG 17</td>
<td>Chloraized Copper Phthalocyanine</td>
</tr>
<tr>
<td>Jenkins Green</td>
<td>PBk 9 / PY 150 / PG 36</td>
<td>Amorphous Carbon Nickel Complex Azo Brominated &amp; Chlorina-Copper Phthalocyanine</td>
</tr>
</tbody>
</table>
Figure K.1: The spectral reflectances of artist paints provided in Okumura's database.
Figure K.1: The spectral reflectances of artist paints provided in Okumura’s database (continued).
Figure K.1: The spectral reflectances of artist paints provided in Okumura’s database (continued).
Figure K.1: The spectral reflectances of artist paints provided in Okumura’s database (continued).
Figure K.1: The spectral reflectances of artist paints provided in Okumura’s database (continued).