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A Diagnostic Exam for the Non-invasive Identification of the Artist's Palette of Pigments

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A Diagnostic Exam for the Non-invasive Identification of the Artist's Palette of Pigments

A dissertation submitted in partial satisfaction of the
requirements for the degree of Doctor of Philosophy

in

Materials Science and Engineering

by

Samantha Stout

Committee in charge:

Professor Jan B. Talbot, Chair
Professor Jacopo Annese
Professor Jules S. Jaffe
Professor Falko Kuester
Professor Joanna McKittrick

2015

The Dissertation of Samantha Stout is approved and is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2015

DEDICATION

To Antonio, my parents, and my dearest grandmother - Nanny Duck.

To Maurizio

EPIGRAPH

Why are we weigh'd upon with heaviness,
And utterly consumed with sharp distress,
While all things else have rest from weariness?
All things have rest: why should we toil alone,
We only toil, who are the first of things,
And make perpetual moan,
Still from one sorrow to another thrown:
Nor ever fold our wings,
And cease from wanderings,
Nor steep our brows in slumber's holy balm;
Nor harken what the inner spirit sings,
"There is no joy but calm!"
Why should we toil, the roof and crown of things?

Alfred, Lord Tennyson

Once more I sit me at the feet of
Thoughts that have never died;
While college memories sad and sweet,
In eternal bond are tied.
Then knowing of me today
From study of We before
I leave the college door.
And the bells in the tower say
"Ding dong, ding dong."
The hour is filled.
I've sung the college song.

Robert Shapiro, Cornell Class of 2004

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The material in Chapter 3 may be presented for publication at a later date.

Chapter 4, in full, is a reprint of the material as it appears in S. Stout, F. Kuester, M. Seracini. "XRF Assisted, Multispectral Imaging of Historic Drawings" Advances in X-ray Analysis, 56, (2012); A. Cosentino, S. Stout, R. Di Mauro, C. Perondi. "The Crucifix Chapel of Aci Sant'Antonio Newly Discovered Frescoes" Archeomatica, 2, (2014); and the conference poster "A comprehensive methodology for the analysis of a 16th century fresco mural" presented August, 2012 at the 1st Gordon Research Conference in Scientific Methods for Cultural Heritage Research, Mt. Snow, Vermont. The dissertation author was a primary investigator and author of these papers.

Chapter 5, in part, is a reprint of the material as it appears in D. Vanoni, S. Stout, A. Cosentino. "ARtifact Conservation: Representation and Analysis of Spectroscopic and Multispectral Imaging Data Using Augmented Reality" Proceedings of the 18th ICOMOS Meeting, Track 5: Emerging Tools in Conservation Science. Florence Italy, (2014). The dissertation author was a primary investigator and author of this paper. Chapter 5, in part, has been submitted for publication of the material as it may appear in the conference proceedings of Digital Heritage 2015: S. Stout, J. Strawson, E. Lo, F. Kuester. The WAVEcam: Ultra-high Resolution Imaging of Paintings Digital Heritage 2015, Granada, Spain. The dissertation author was the primary investigator and author of

this paper.

The material in Chapter 6 may be presented for publication at a later date.

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S. Stout, F. Kuester, M. Seracini. "XRF Assisted, Multispectral Imaging of Historic Drawings" Advances in X-ray Analysis, 56, (2012).

A. Cosentino, S. Stout, R. Di Mauro, C. Perondi. "The Crucifix Chapel of Aci Sant'Antonio Newly Discovered Frescoes" Archeomatica, 2, (2014).

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FIELDS OF STUDY

Major Field: Materials Science and Engineering (Cultural Heritage Diagnostics)

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Studies in Art History
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ABSTRACT OF THE DISSERTATION

A Diagnostic Exam for the Non-invasive Identification of the Artist's Palette of Pigments

by

Samantha Stout

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2015

Professor Jan B. Talbot, Chair

The fields of conservation science and scientific analysis for cultural heritage research are typically characterized by limited studies of unique artifacts. This research proposes a change to the current approach by use of a standard scientifically-based diagnostic approach similar to that followed in the field of medicine.

The non-invasive identification of the artist's palette of pigments is the focus of this research in the development of the first diagnostic exam for the assessment of painted artworks. The existing techniques of technical photography and X-ray fluorescence spectroscopy were applied in a dual-technique protocol designed especially to

make the analysis fast, reliable, and low-cost. The exam methodology incorporated a new systematic approach for data processing, combining the information from the two complementary techniques for accurate and consistent pigment identification results.

The exam methodology was implemented in three different scenarios: a historical drawing, a fresco mural, and wall paintings, each of which served as a test for the protocol in a field environment.

As a member of an interdisciplinary team in the Qualcomm Institute's Center of Interdisciplinary Science for Art, Architecture, and Archaeology (CISA3), advanced tools for advanced implementation of the diagnostic exam were developed and informed by the field scenarios. A platform for data visualization was created using an augmented reality tablet device to provide data contextualization for the acquisition and analysis workflow and improve the retention of important metadata. A robotic platform was also adapted from a 3D printer to provide automation accelerating the data acquisition phase of the exam.

Finally, two experiments were designed to test the capabilities of the diagnostic exam on known samples that were more complex than single pigment swatches and more closely resembled an actual artifact. A mock-up oil painting and controlled mixture and layering scenarios were used as test samples to qualitatively evaluate the performance of the exam to deliver accurate results. This research presents a data-driven approach to preventative conservation that is scalable and suited to the variety of users in the field.

Introduction

There are many sophisticated ways to examine the minute material characteristics of a painting, and the research is growing at an incredible rate [ref?]. An idea that is still seen as radical is that the field of conservation can be practiced in a way that is more analogous to medicine; meaning that the health of a painting can resemble our own human health, and a diagnostic approach including routine check-ups can be implemented.

This idea largely remains a foreign concept to heritage stakeholders, conservators, and restorers; however art diagnostician, Maurizio Seracini, has argued for it for several decades. Seracini, who has operated the diagnostics company Editech since 1977, has built a philosophy on the diagnostic evaluation of the state of conservation of works of art, architecture, and cultural heritage that stems from his formal study of medicine in addition to biomedical and electrical engineering. Early on he determined a need for a form of clinical chart containing all the relevant information on the work being studied, including details of analytical exams and their results. It was intended that the chart be updated over time, and that its contents form the basis of a prognosis for the state of health of the artifact that was in turn supported by the data collected. Seracini‘s next tenet was that any intervention should also have a rationale stemming from the prognosis in the chart.

Currently, the modern conservation lab is an interdisciplinary workspace. Many practitioners have multiple competencies, which range from manual artistic and hand-iwork skills, to knowledge of chemistry, history of art and anthropology. Experts in analytical chemistry, materials science, nuclear physics and biology are frequently called upon for their highly specialized knowledge in a certain analytical technique or material class or object; though this usually happens only when the need arises, as determined by the core conservation or curator team. Networks have begun to branch out to connect expertise with artworks in need, and more encompassing multi-technique studies are carried out internationally on artists and materials scenarios, addressing a wide array of risk factors for degradation processes that affect a large portion of artworks.

The above efforts represent great progress and show the true merit obtained by applying the scientific method as a primary approach for the study of the state-of-conservation of paintings. These are advances to the field that particularly stand out when compared with the typical restoration practices of the 19th century. However, apart from most major museums having a dedicated x-ray facility, it is still apparent that conservation could benefit from a diagnostic approach that borrows key traits from medicine. Overall, preventative medicine and preventative conservation are much alike. Both focus on maintenance and stabilization of environmental effects, and both require some form of time monitoring to take place and provide a feedback loop in order to measure the change in state of health. This methodology is scarcely presented in any of the current research trends, and would represent a theoretical and philosophical deviation from the current direction of research, one which has followed famous or renowned artists, benefited from traditional and myopic funding schemes, or delved into the enticing rabbit hole of proof of authenticity studies.

It is proposed that conservation would benefit from a diagnostic approach, including a reliable way to measure certain vital signs. It has been established that there is an open space for the research put forth by this dissertation, which has the unique goal of developing a routine examination of paintings that offers both visual (imaging) and materials information and may be widely adopted as a standard diagnostic practice. The chemical imaging methodology detailed here has been designed to be an efficient and reliable way to document the state of conservation of paintings and determine the palette of pigments used by the artist and can be performed in a variety of examination scenarios. In addition, several accompanying tools have been explored that serve to complement the primary task of data acquisition and analysis, affording the user an agile workflow and facilitating the retention of metadata and integration of primary data with datasets from other techniques.

It has been proposed that the methodology guiding the assessment of cultural heritage artifacts and their subsequent conservation take useful inspiration from the practice of medicine, as motivated by the work and mentorship of Maurizio Seracini. As follows, the diagnostic examination for the identification of pigments developed in this dissertation has been designed to fulfill the role of helping to define the anatomy of the work of art and assess its vital signs in a readily adoptable and standardized way.

This dissertation serves as a critical exploration of the best way to acquire and transfer key details on the state of conservation and material components of paintings into the digital clinical chart designed to serve as a repository for such data. As the nature of the intended field of application is very much interdisciplinary, the experience of the doctoral trainee, as well as, the nature of collaborations and case studies carried out was also interdisciplinary.

Chapter 1

Introduction and Objectives

An intimate knowledge of the materials present in a work of art, specifically a painting, can be of extreme utility and value, for several reasons. The first is preservation based, to plan to protect the art, mitigating any current vulnerability; as well as, to monitor and deter degradation from occurring in time. The second is that this information could be key evidence in the case for demonstrating the authenticity of the work. And the third is the ability to inform and stimulate new knowledge in other disciplines, such as art history, sociology, or geopolitics based on the provenance of the materials, the artists palette, and technique of execution. All three of these realms can be informed through the diagnostic technical evaluation of the work of art, which is usually undertaken via the collaboration of multidisciplinary team members made up of conservators, restorers, art historians, curators, and scientists.

It so happens that usually an expert in chemistry or materials science is called in to work on the team to carry out requested exams, performing analysis on small micro-samples, or point-based non-invasive spectroscopies on the work itself. In most scenarios, time with the work of art is severely limited, and access is in some way controlled. After the tests are run, the materials scientist is then tasked with interpreting the data and explaining the results to experts in other disciplines. At the highest levels of this type of research most team members have interdisciplinary skill-sets, facilitating the interpretation stage with a scholarly dialogue. However, in a typical museum setting where technical exams may have only been adopted relatively recently, the staff may have varying levels of scientific training or expertise, such that implementing a standardized procedure for the acquisition of characteristic material data and then ensuring comprehension of the full set of results from a multi-analytical approach becomes a practical challenge.

More often than not, conservators and restorers have some background in chemistry. Conservation scientists likely have had more formal training courses in analytical techniques, specifically applied to works of art. However, for most practitioners involved in conservation based decision making, seeing a few spectra whose "fingerprints" match with databases to identify pigments, doesn't translate to an understanding of the work of art, especially when analyses are point-based or when complex mixtures are involved. In the art world, every artifact is unique and every sample is an unknown matrix. On the other side of the coin, scientists often lack any formal preparation in art history or the practical workings of artist's chemistry. The information that comes with a conservator's practical expertise can be vital to illuminate particularities that emerge when unknowns from painted media are studied.

The exam methodology developed through this dissertation is aimed at providing two key necessities in cultural heritage diagnostic survey: providing materials information that is global (not limited to a set of finite areas), and providing information that is visual, and therefore can be read and interpreted by specialists from various disciplines. The ideal methodology is demonstrated through a series of case studies and additional experiments serve to provide qualification and quantification metrics, as well as, to begin to tackle the analytical interpretation problems posed by common mixtures. The "multi-technique approach" has been widely adopted by leading researchers in the field, but as of yet, no one has worked to suggest a standardized instrumentation, experimental setup, and procedure that has the chance of achieving ubiquitous use while being adaptable to advances in technology.

The intention of this dissertation is to offer technical solutions, methodological clarifications, and experimental scenarios that build upon the state-of-the-art, from the perspective of a materials scientist who has become a truly interdisciplinary trainee in cultural heritage diagnostics. The presented work provides a summary of a standardized diagnostic exam designed for the non-invasive identification of pigments present in a work of art as one step toward a large-scale data-driven approach to preventative conservation, and as an initial research on how to arrive at a practical method for chemical imaging.

Chapter 2 reviews the background literature and provides a general understanding of the ideas and prior research forming the framework and main themes of the dissertation. This field of Cultural Heritage Diagnostics will be defined and the typical goals of research in this discipline will be discussed in Section 2.1. The remainder of chapter 2 provides a review of the diagnostic techniques themselves, and is separated into Materials Analysis (Section 2.2) and Imaging (Section 2.3), the two main components of the Chemical Imaging Methodology at the heart of the dissertation. These sections walk the reader through the basic operational parameters of a diagnostic exam carried out on a painting using the techniques, how they work, and what information is expected to be obtained. Then, the reader is referred to an example of a state-of-the-art implementation of each technique from the scientific literature. Chapter 2 serves to acquaint the reader with the many possibilities for diagnostic assessment of a painting, and provides the first ideas of what trade-off's inherent to the techniques themselves may be involved when practical diagnostic exams are carried out.

Chapter 3 presents the methodological design and protocol for the diagnostic exam for the non-invasive identification of the artist's palette of pigments. The design criteria and building blocks are introduced first along with the description of a typical field-work scenario. Then, the exam workflow is detailed in full. Section 3.2 reads like a guide manual and covers Data Acquisition (3.2.1), Data-storage and Post-processing (3.2.2), and the Data Interpretation (3.2.3). Section 3.3 presents an improved flowchart method, which builds upon the work of Cosentino in [4].

Chapter 4 contains three implementations of the diagnostic exam in a field setting. The first is the analytical study of the preparatory drawing for "The Adoration of the Magi" by Leonardo da Vinci, section 4.1. Next, in section 4.2, the fresco by Giorgio Vasari, "The Battle of Marciano in Val di Chiana" has been studied as part of the overarching "Search for the Battle of Anghiari", a research project that Prof. Seracini has directed since 1975. In the 2011 edition of the research project, an interdisciplinary team of engineers at CISA3 collaborated to perform endoscopic investigations on the East wall of the Hall of the 500 in Palazzo Vecchio, Florence. During the course of this research project, which was documented by National Geographic, there was opportunity to survey the Vasari fresco and apply the diagnostic exam developed in this research. The third field application (4.3) involves a particular chapel in the town of Aci Sant'Antonio, Sicily, where a cycle of wall paintings was discovered in 2012 as a result of restoration work. In this case the diagnostic exam was again applied, and the results were conveyed to the parties responsible for planning the conservation procedures.

Chapter 5 presents advanced applications of the diagnostic exam where new tools for implementation have been developed. The first part covers the WAVEcam robotic hybrid platform; a modular mobile instrument which incorporates automation into the implementation of the exam methodology. The second part of chapter 5 presents an augmented reality tablet platform for data visualization, contextualization, and retention of metadata.

Chapter 6 includes two cases studies designed to evaluate the performance of the diagnostic exam. In section 6.1 an oil painting called the "Pratt Madonna" provides a simulation of a Renaissance painting that has been heavily restored, containing both historical and modern pigments. This painting has been previously studied [7] and this section adds the XRF analysis to the existing work using the improved flowchart developed in section 3.3. Section 6.2 presents a second case study designed to further investigate the performance of the diagnostic methodology for pigment mixture and layering scenarios.

Chapter 7 concludes the dissertation, reviewing the primary tenets of the diagnostic exam methodology and discussing the impact on the field. Pathways for future research are suggested, including a potential pathway to a new signal processing based methodology for chemical imaging.

1.1 Cultural Heritage Diagnostics

Cultural Heritage Diagnostics describes the overarching field in which technologies are employed to examine cultural artifacts in order to answer questions about their material histories, techniques of execution, and state of conservation. The field is usually best explained through analogy to the field of medicine. The artifacts are the patients, presenting with unique anatomies, and plagued by pathologies leading to their decay. Then comes in the doctor of general medicine, the diagnostician, who can suggest a full-workup and propose additional more specific exams based upon further findings or needs. Specialists are then involved in a multidisciplinary, team based approach to holistic medicine. The methodological approach of cultural heritage diagnostics will be described in this dissertation primarily using case studies where the artifact is a painting.

1.1.1 Analyzing Cultural Artifacts

This section will briefly address some key particularities with regards to the investigative analysis of cultural heritage artifacts. Firstly, there is an overwhelming need to operate in a non-invasive manner. Items are unique, one-of-a-kind, precious and priceless. Every item has its own history, and most likely few details will be available on the historical alterations, restoration procedures, and environmental conditions throughout the life of the artifact. The materials of the painting have been interacting with each other in ways that are only somewhat understood and can have different rates of decay or mechanisms that are intertwined with one another [8]. Specific details on the techniques of execution use by the artist may be known or unknown.

1.1.2 The Digital Clinical Chart

Continuing with the analogy to medical practice, the digital clinical chart (DCC) serves as a repository for all the information known about the artifact. It is intended that the DCC will continue to be updated and annotated throughout the lifetime of the artifact. Figure 1.1 depicts a schematic representation of the contents of the DCC.

Here we see the content broken up into two major parts, the art historical research and the scientific research. It must be reiterated that these are of equal importance, as the historical information is vital to interpret the results of the scientific exams and to evaluate and assess the nature of the work of art and its distinct value. The records (if there are any) relating to the history of prior restoration efforts are always of particular interest, as these may help discover material incongruities or areas which are likely to present subsequent conservation issues. The scientific research section of the DCC is then divided into two categories, diagnostic imaging, and analytical diagnostics - indeed, the two main components of the chemical imaging methodology being developed here. Diagnostic imaging is an overarching term used to describe the many practical ways that the optical properties of materials, intrinsic band gaps, reflectance spectra, and transparencies in certain regions of the electromagnetic spectrum, can be probed and investigated. These include the practice of technical photography, imaging in multiple

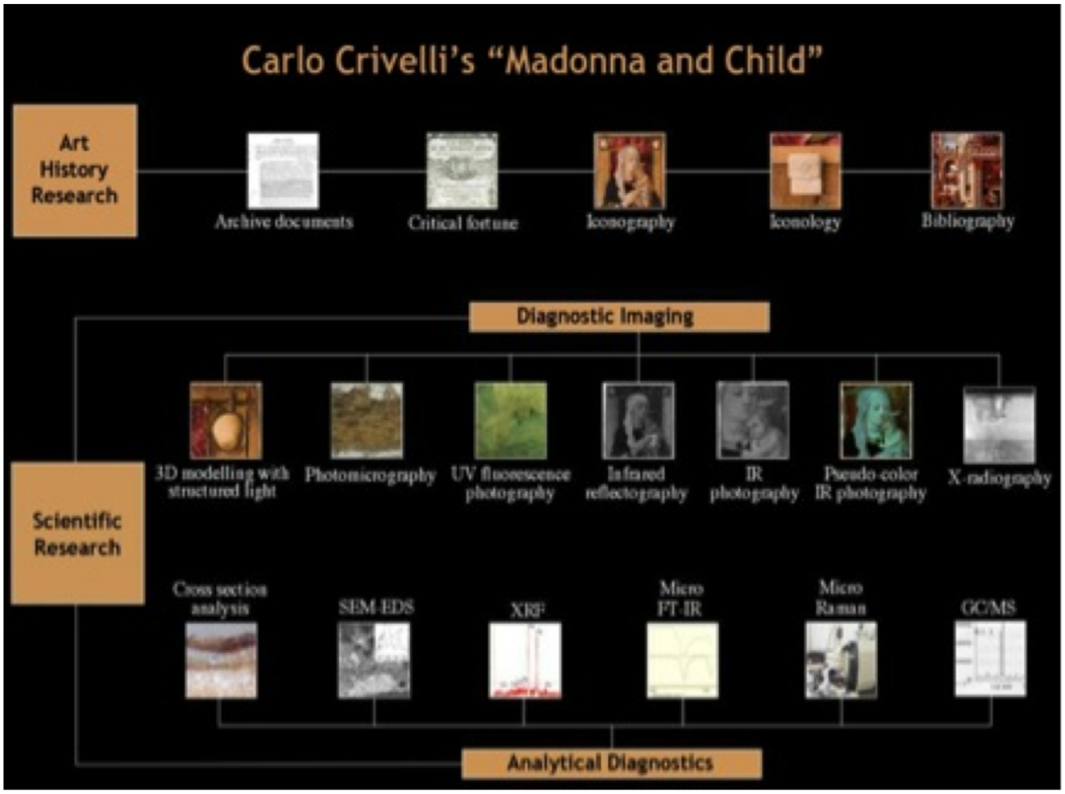

Figure 1.1. Schematic diagram of showing the structure and content of the digital clinical chart [1].

bands, multispectral and hyperspectral imaging, which will be introduced and reviewed later in this chapter (sections 2.3.2 and 2.3.3). Analytical diagnostics covers the many exams that provide chemical analysis, e.g. elemental, molecular, vibrational, etc. and can include the analysis of micro-samples typically embedded in a polystyrene resin and prepared as polished cross-sections. These will also be described and reviewed in a section of this chapter (2.2).

1.2 Objectives of the Diagnostic Exam for Pigment Identification

The objective of the dissertation was to develop a non-invasive diagnostic exam that could be used to analyze paintings in a standardized way and produce data that could be used to characterize them. It was pertinent that this exam be able to be adopted on a large scale by a wide variety of users. The identification of the artist's palette of pigments was chosen as the goal for the exam. This was a good target because the information obtained would be meaningful from a conservation and art historical standpoint, and a common methodology for this specific goal has not yet been systematically applied in the field.

Objectives for the diagnostic exam were defined in the following way.

- The exam should be efficient. The effort required to follow the procedural recommendations should give an equal trade-off with the quality and usefulness of the data obtained. The time required should also reflect this balance, as well as the notion that the intention is to allow implementation on a large scale.

- The exam should be reliable. Data should be able to be reproduced and the results should be able to be trusted. This will be accomplished through applying established techniques whose instrumental specifications and standard operating procedures are then adapted to fit the other exam objectives.

- The exam should be adaptable. There is no requirement that everyone obtain instruments or equipment from a single manufacturer, instead only general specifications will be outlined. This will also allow the exam to be updated appropriately when new technologies come onto the market, and allow each user to find the equipment at a level that fits their budget.

- The exam should be standardized to produce data that are comparable from one artifact to another and from one researcher to another. Even if the techniques are carried out using a different brand or model instrument the procedures for processing and interpretation of the data should serve to remove any effect. Common methodological practice of the individual techniques and state of the art advancements in data processing will work to achieve this.

- Lastly, the exam should be accessible. It should be accessible from budgetary, personnel, and infrastructure standpoints. It is the objective of this dissertation that the diagnostic exam can be adopted by any institution charged with preserving painted artworks.

Chapter 2

Background

2.1 The Analysis of Paintings

2.1.1 The Anatomy of a Painting

A practicing diagnostician must have an intimate knowledge of the anatomy of the subject matter, that is the patient, in order to proceed wisely with examinations and diagnosis. In the case of paintings this general review will cover the most basic components of a typical painting, however the technique of the particular artist, time period, or school could have significant influence over the anatomy of the work of art, and thus art historical expertise should be consulted whenever possible. A good basis in painting anatomy and materials is available from [2].

The painting begins at the support, which is the physical basis for adding the painted layers. We know this usually as canvas or wooden panel. (In the case of manuscripts and drawings it is the paper substrate, vellum, or parchment.) Canvas is extended over a wooden stretcher, pulled taught and then affixed. Then, a layer of size is added. Size is usually a mixture of animal glue (typically rabbit skin), and functions to prevent the following layers from leaking into the support and weakening it in any way. Next, a ground preparatory layer is prepared and applied; the materials and style of which varied throughout time and space and between schools. Typical grounds are

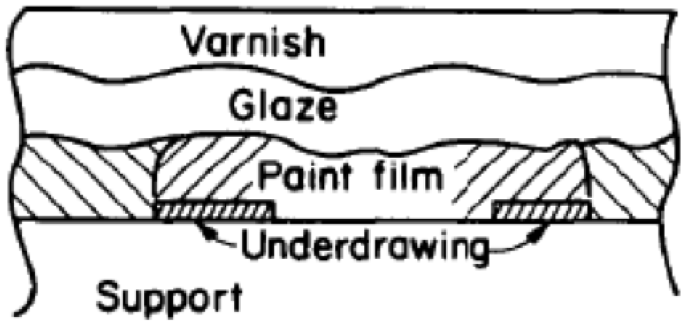

Figure 2.1. Schematic diagram of a cross-section of the painting, from [2]

made from gesso (calcium sulfate), calcite (calcium carbonate), and a mixture of either of these with earths (ochre) for a red colored ground. Some painters also were known to use lead white in their preparatory layers. [2]

The first signs of the figures included in the work can be in the form of underdrawing, usually executed with charcoal, by pouncing sinopia (earths), or perhaps metal point. The underdrawing is the first sketch, and can potentially be transferred from the preparatory sketch (made on another piece of paper) using the pouncing method. After the underdrawing is laid out, texture may be added by incising the work along the lines (this is especially true in the case when gilding will be applied). Then, the painted layers are applied on top, effectively covering the underdrawing and becoming the work of art we know when we see it. Lastly, varnishes or glazes may be applied for the final visual effect, or to protect the painted layers. Not all artists apply a varnish layer, and sometimes conservators or restorers remove them or apply, or re-apply them years later.

The material constituents of paint

Paints as we have come to know them have evolved over time and this review will take an overall approach, though concern itself mostly with the historical way of making pigments during the time period surrounding the Renaissance, from the 14th to

Elements Used in Pigments

Name	*Symbol*	*Atomic No. (Z)*	*Pigments*
Carbon	C	6	carbon black, calcium carbonate
Oxygen	O	8	lead oxides, chromates
Sodium	Na	11	lapis lazuli, French ultramarine
Aluminum	Al	13	ultramarine, cobalt blue
Silicon	Si	14	smalt, quartz
Phosphorus	P	15	cobalt yellow
Sulfur	S	16	lithopane, vermilion
Chlorine	Cl	17	patent yellow, platina yellow
Titanium	Ti	22	titanium white
Chromium	Cr	24	chrome yellow, veridian
Manganese	Mn	25	manganese blue, raw and burnt umber
Iron	Fe	26	hematite, yellow ochre
Cobalt	Co	27	cobalt blue, cobalt yellow, cerulean blue
Copper	Cu	29	azurite, malachite
Zinc	Zn	30	zinc yellow, zinc white
Arsenic	As	33	orpiment, emerald green
Selenium	Se	34	cadmium red
Cadmium	Cd	48	cadmium red, cadmium yellow
Tin	Sn	50	lead–tin yellow, cerulean blue
Antimony	Sb	51	antimony vermilion
Barium	Ba	56	lithopane, barium yellow
Mercury	Hg	80	vermilion, cinnabar
Lead	Pb	82	lead white, Naples yellow, red lead, litharge

List of elements used in pigments by name, symbol, atomic number (Z), and pigment name.

Figure 2.2. Table showing the major elements in common pigments. Pigments considered to be 'historical' are underlined, from [2]

18th centuries, before the Industrial Revolution introduced new practice. During this age, painters prepared their own mixtures in their workshop and did not buy paint that was commercially manufactured and sold in tubes, as we are accustomed to today. Cennini provides the most widely circulated reference as to the practice of the time [9], though each workshop most likely experimented with variations on his recipes.

Basically put, the painted layer consists of the mineral pigment and the binding media, which allows it to be spread across the surface. The mixture begins as a liquid and is intended to remain permanently as a solid once the drying process is complete. Binding media are organic in nature, while the pigment material is usually an inorganic mineral. A comprehensive reference for historical pigments can be found by consulting [10].

The pigment must be physically or mechanically ground so that the granules assume a relatively uniform size and are spread evenly throughout the binder. This will result in the best optical properties; see next section for more details.

Solvents, extenders, catalysts, or primary materials make up a potentially long list of other materials that may be present or may have been added to the basic paint mixture. Lead was known to accelerate the drying process of linseed oil and thus can often be found when analyzing historic paints, even when the main pigment component is not lead based. Pigments prepared for painting "al fresco" must be compatible with the alkaline environment of the wet plaster, which hardens according to the chemical reaction in equation 2.1.

$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l) \tag{2.1}$$

When a paint with binding media is instead used on a wall painting the technique is known as a secco or dry, since it will not bind chemically with the plaster, but instead become a new surface layer. These types of touch-ups are common on frescoes, especially in the blue and green regions of the painting, as these pigments were incompatible with the true buon fresco form. Information on mapping areas carried out "a secco" is of pertinent interest to conservators of wall paintings. Chapter 4.3 describes a case-study analysis of wall paintings, which include portions completed al fresco and a secco made with pigments laid in a binding medium (likely egg yolk tempera).

The optical properties of painted layers

This section will address four main aspects of paint, how they produce color, how we evaluate and determine the color, how the color may change over time, and how

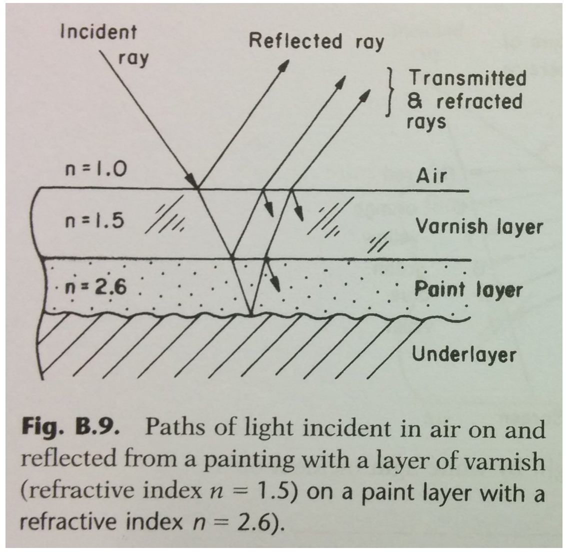

Figure 2.3. Schematic diagram of light interacting with a cross-section of the painting, from [2].

colors are formed in mixtures of more than one pigment.

When light interacts with the painted layer it may be reflected, refracted, absorbed or scattered. Each of these effects plays an important role in the perception of the color by the human eye. The particular wavelengths of light that are reflected determine the color we see; the refractive index contributes to the hiding power or opacity of the paint; and the extent of scattering is affected by the the pigment particle size – too small and the intensity of the color can be lost, resulting in a dull grayish effect. (Optimal particle size is between 20-80 microns.) In addition, the response of a pigment to light contains information based upon both intrinsic and extrinsic factors that correspond to the material itself and may be used to identify and characterize it.

The text "The Physics and Chemistry of Color" breaks down the causes of color into five categories: vibrations and simple excitations, transitions involving ligand field effects, transitions between molecular orbitals, transitions involving energy bands, and geometrical and physical optics [5]. Generally, many pigments fall under the category of transitions involving ligand field effects, with organic dyes involving transitions between

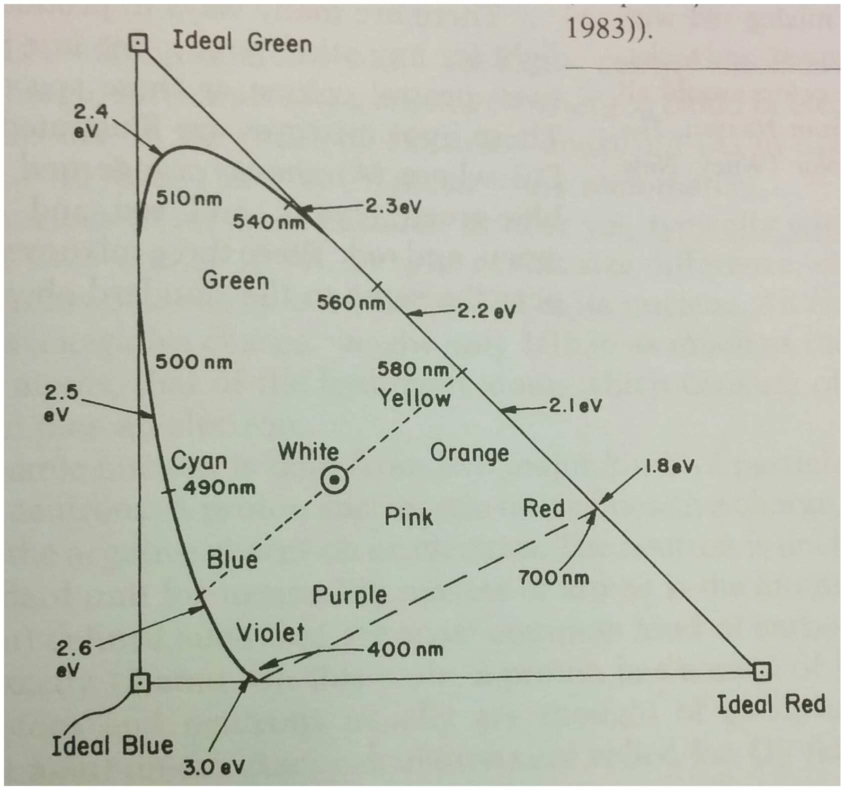

Figure 2.4. CIE space annotated with energy values, from [3].

molecular orbitals, and certain pigments, such as cinnabar / vermilion (HgS), possessing semiconductor properties and thus producing color via energy band transition. The text also devotes a chapter subsection to the Raman scattering effect, which is listed as a geometrical optical effect [5].

Though pure pigments have been characterized, and library databases containing their UV-VIS-NIR reflectance spectra have been created, the optical response of pigment mixtures or overlapping pigments can vary considerably from the pure pigment. The paper Identification of pigments by multispectral imaging; a flowchart method depicts a layering scenario using three blue pigments with different optical properties and the effect on the results of technical photographic images [4], (Fig. 2.5).

Transparencies in certain regions of the UV-VIS-NIR spectrum can cause overlapping pigments to exhibit a different appearance from the characteristic response of the

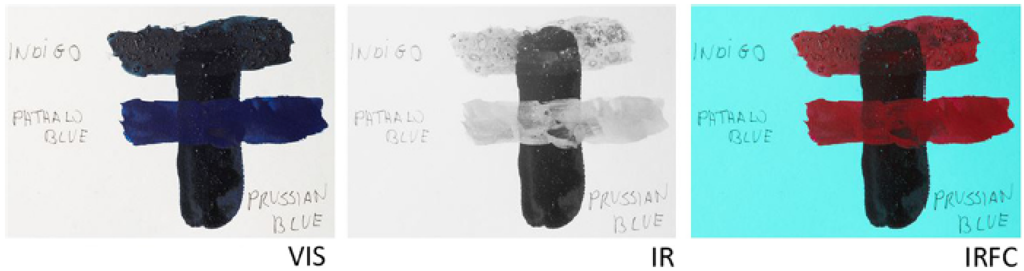

Figure 2.5. Examples of the effect of overlapping pigments on TP analysis, from [4].

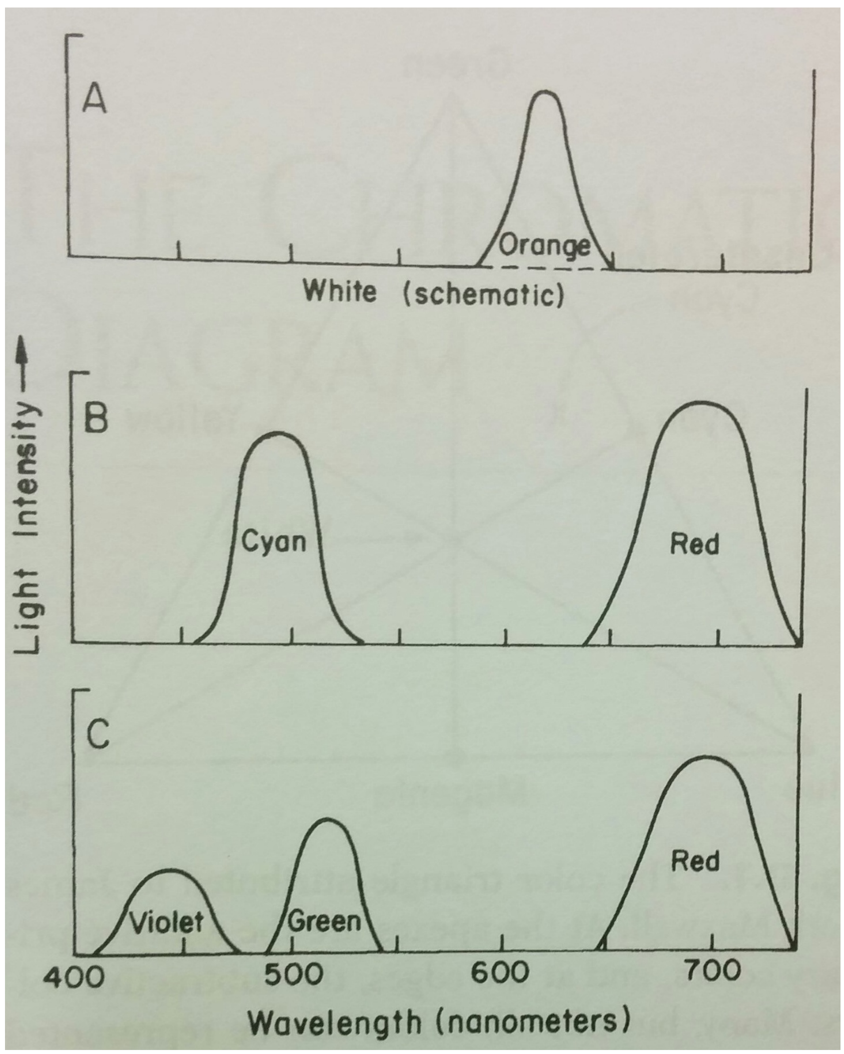

Figure 2.6. Examples of the spectral response of metameric colors, from [5].

single pigment, as compared to the pigments checker swatch standard. This could complicate the pigment identification process for a real painting scenario, and the author, aware of this, claims that TP and the flowchart method can only offer a tentative conclusion for pigment assignments. Remedies to avoid false identification will be addressed through the design of the methodology for the diagnostic exam presented in this dissertation.

The subject of colorimetry is concerned with objectively representing color in a way that correlates with human perception of that color. Colorimetry and CIE space provide a framework of variables and relationships arranged so that color can be measured and reproduced reliably. The text published by Wiley is a comprehensive reference on colorimetry and CIE space [3]. A thorough knowledge of the working principles of colorimetry is useful to prevent mistakes in color identification and pigment assignment based on interpretation of visual data such as technical photography images. It is also useful to understand the necessary calibration and standardization procedures that must be carried out.

When a digital camera captures color, the light passes through a Bayer filter before reaching the sensor, and is thus separated into the Red, Green, and Blue (RGB) channels. Each filter has a slightly different response curve for accepting wavelengths. When the image is imported into the computer, the RGB values for each pixel are defined (0 to 255 for an 8-bit image, and 0-65536 for a 16 bit image) can be output, and effectively these determine the color we see reproduced on the monitor. Numerical values for RGB represent one way to definitively assign color. Acquiring images using the camera RAW file format, a color-checker standardization card, and then converting the images using the digital negative (DNG) format calibrated to the sensor, lens, and lighting scenario, is the proper way to standardize the representation of colors in digital photography according to the AIC [11].

There are some things to keep in mind from the standpoint of the conservation scientist and the materials scientist, in order to put the evaluation of color in perspective in the chemical imaging methodology. Perceived (and photographed) color depends upon the illumination source. Color can result from an additive effect of the wavelengths reflected, or by a subtractive effect (i.e. by those absorbed). And, as mentioned previously, transmittance properties can have a significant effect when layers are involved. Standard practice for color management and capturing the diagnostic images used to evaluate a work of art will be discussed in Chapter 2.3.2 on Technical Photography.

The Kubelka-Munk (K-M) theory of turbid media was developed in 1931, the same year as CIE space. It predicts the spectral reflectance of a paint coating based upon the optical properties of each of the parts of the mixture. Zhao has investigated the effects of thickness and translucence on the performance of K-M theory, and others have used it for applications as varied as correcting FTIR spectra. The application of K-M theory also gave way to attempts to perform spectral un-mixing, essentially the reverse procedure of trying to deduce the components of a mixture based on the spectral behavior of the whole [12].

Perhaps what is most concerning to conservators and stakeholders in charge of protecting our art and cultural heritage for future generations is that the color of some pigments can change over time. Some changes have been documented for many years now, and were known to exhibit this behavior, being called "fugitive" in the case of dyes known to fade over time. In some cases, such as with eosine lake (geranium red), this discouraged artists from using the particular pigment. In other cases color changes occurred for different reasons, and on different time scales, which did not discourage the use of the pigment. For example, azurite (blue pigment) can change into the chemically similar, yet green, malachite in the presence of certain binders, over time, or when exposed to excessive moisture. Vermilion (red, HgS) has also been documented to turn black under specific conditions [8]. It must be iterated that not all color changes are well understood and that research is still progressing to characterize the extent to which paintings change in color due to effects of the pigment itself, (as opposed to yellowing from an aging varnish layer). One example of current research is on Cadmium pigments and their color changes [13]. Since, many pigments obtain their color due to ligand field effects, they can be quite sensitive towards impurities and disruptions in the coordination and charged state of the atoms, which can be effected as the binding media undergoes changes due to drying/aging or external factors such as changes in relative humidity or exposure to ultraviolet light.

The appearance of the entirety of a painting can also change due to the aging processes of the varnish layer, if one has been applied. This is most often described as a yellowing effect and is frequently cited by conservators as the impetus for cleaning procedures, the removal of old varnishes, and the reapplication of a new varnish layer. Conservation practice with regards to removing prior varnish layers has fluctuated over the years based on many factors; e.g. the original intent of the artist, the ability to safely selectively dissolve the varnish media without affecting the painted layer or binding media, the general condition of the painting, the ability to read the subject matter, and the philosophy of the particular conservation workshop. Paintings with thick and obscuring varnish layers are intentionally left out of the discussion of the methodology described in this dissertation.

Documentation and quantification of color, an extremely important characteristic in the art world, can be a promising first step towards materials identification. While the spectrophotometric response of many pigments and colorants is indeed a characterizing feature, representing intrinsic properties of these materials (morphology, crystallography, coordination number, ionization state), in the case of paintings it is most likely that too many factors are at play to positively identify all of the pigments used or to provide conclusive proof that a particular pigment has been used with imaging techniques alone.

2.1.2 Diagnostic Approach

The practitioner workflow developed by Maurizio Seracini and implemented at Editech Srl. represents a pioneering approach to cultural heritage diagnostics. After analyzing more than 3000 works of art, Seracini has encountered a vast variety of materials and state of conservation scenarios. His method will be briefly recounted here in order to understand the standard of practice, and to make clear the exact placement and function within the chemical imaging methodology described in this dissertation [1].

First the painting is examined by eye in three dimensions. Key factors relating to material history and state-of-conservation are noted, including: the condition of the support, stretcher, relining of the canvas; the use of finishing nails, and any markings or inscriptions (representative list). Then, the painted surface is analyzed under the microscope as described in section 2.3.1. Next, the painting undergoes technical photography as described in section 2.3.2. It is important to keep these steps in order, as information gained in previous steps will go on to inform a careful analysis and interpretation of the data obtained in the subsequent steps. The Technical Photography (TP) step is the bare minimum for the documentation of state of conservation, and ideally this exam should be repeated at regular intervals (e.g. once a year to once every five years) to check the artifact and note any changes. TP should be taken before and after restorative interventions are carried out. Additionally, Seracini has mastered the acquisition of x-radiographs of paintings. Described briefly in section 2.3.4, the x-ray exam will not be included in the scope of chemical imaging discussed in this dissertation.

One major goal of the state-of-conservation assessment is to determine the palette of pigments used by the artist. Palettes are important characteristics of artist school and technique, and they evolve over a particular artists lifetime as the artistic landscape changed, and as new materials became available. For paintings made with historical pigments (e.g. old masters, pre-industrial revolution), TP can identify the presence of most, but not all, of the pigments [14]. Therefore, the diagnostic exam for pigment identification employs an additional technique to help define the palette. Portable XRF (pXRF), though only a point-based technique, is portable and non-invasive. Demonstration of the improved flowchart method in section 3.4 will show the added benefit of the XRF analysis in positively identifying pigments, including which pigments remain undetectable or inconclusive.

The diagnostic approach presented in this dissertation will build on the work and methods of Seracini, Cosentino, and Delaney [1, 15, 16]. It will also take into account the specific objectives defined to address the needs of the cultural heritage and conservation communities. The methodological design must take into account the intended user and accommodate a practical and ergonomic workflow, so that all the necessary steps are reliably accomplished in the correct manner without undue strain. An agile method will have the advantage of higher adoption rates. The amount of energy required to implement and conform to a new standard operating procedure must be favorable. Another key factor in encouraging adoption is not to make the barriers to entry unnecessarily high in terms of cost for equipment and operation. Therefore, low-cost equipment has been selected over potentially more sophisticated, but less accessible techniques. The real advantage will be when standardized results are able to be collected on a very large scale, enabling the comparison across artists, genres, and time periods directly from the conservator’s condition report, without needing to account for difference in exam methodology or equipment. Lastly, the method should include some assessment about the quality of the results obtained that can be made available independently of the user’s expertise.

2.2 Materials Analysis

This section will review the common techniques included in a preliminary diagnostic survey and present less common techniques as advanced tools to answer particular questions. The following chart will be used for guidance.

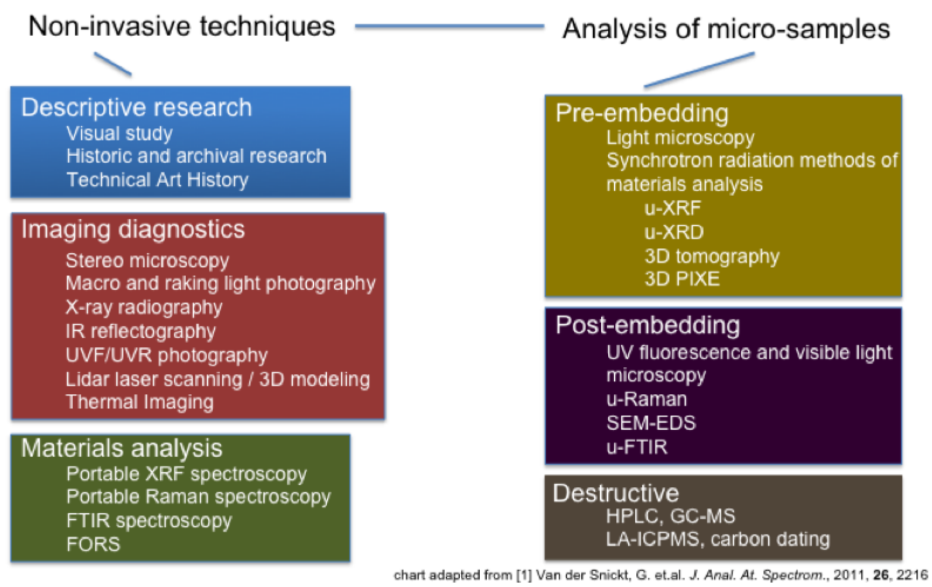

Figure 2.7. The materials characterization toolbox.

It should be noted that almost always, the stakeholders must expressly approve such materials analysis before it is carried out. At the moment, these exams are not simply routine practice. This is due to the time, money, and personnel requirements that must be balanced by collection holders and museum laboratories. Artifacts typically undergo analysis if they will be displayed in an upcoming exhibition, loaned to another institution, or are found to be in a grave state of conservation (potentially after transfer of ownership or a disaster event). Otherwise, it is safe to say that the size of collections often prohibits routine assessments of state of health for ordinary (not excessively prominent, famous, or rare) artifacts. In the case of paintings, this dissertation aims to propose a methodology that would help to increase the standardization and implementation frequency of such a routine examination, thus making adoption ubiquitous by the collections stakeholders. Managed in the correct way, with organized data storage and agile sharing platforms this would have far-reaching implications on the fields of paintings conservation and art history.

To quote the presentation of the Keeper of Conservation and Scientific Research at The British Museum (given 21st February 2014 at the Smithsonian Institution), whether materials analysis is undertaken on an artifact depends upon the "cost and availability of equipment or analysis." [17] Factors to be considered include: is the method routine and part of the basic museum toolkit? can it be done 'in-house' or must it be performed through a collaboration with another center; and finally, must a sample be sent out to a dedicated lab where analytical services are purchased? Then several other factors are weighed, such as: the sample size, visibility, and aesthetic impact; the long term impact on the object; the significance or representativeness of the results; the certainty of obtaining a result; the quality of the questions and the researchers experience; and lastly, the novelty of the method and the potential effect on future research. [17]

2.2.1 Non-invasive Analysis

It is of ethical concern to prioritize non-invasive research when documentation, analysis, and characterization are carried out on cultural artifacts. Depending on the stakeholder or governing body, sampling may be allowed under certain circumstances or may be prohibited outright. Regardless, opportunities to obtain information using non-invasive methods of analysis should, in most cases, be exhausted before proceeding to an analytical method requiring a destructive sample. The case where an invasive technique is required to obtain certain information in order for a necessary conservation treatment to proceed, would be an exception.

A list of non-invasive techniques is shown in figure 2.7, broken down into three categories: descriptive research, imaging diagnostics, and materials analysis. For the purposes of the discussion here it will be assumed that the lighting methods used in imaging diagnostics do not harm the artifact. According to several sources, this is a valid assumption [7, 11]. It is also pertinent to note the semantics of using the term non-invasive versus non-destructive. This is to accommodate potential changes or alterations on the molecular or atomic scales that are too small to be noticeable without sophisticated laboratory equipment or synchrotron techniques, are too infrequent, or have too small of an effect to be consequential, both visually and with regard to the current and future state of health and conservation of the artifact. Several studies have assessed the impact of many of the analytical techniques in the table in a rigorous fashion to assuage the concerns of artifact stakeholders [18]. Furthermore, this is a topic most fervently addressed at specialized conferences and meetings since it is sensitive and somewhat open to debate.

Non-invasive techniques for materials analysis are usually common laboratory (or bench-top) spectroscopic techniques, non-destructive in principle, that have been adapted to become mobile or portable. In today's age it is possible to take these instruments for granted, however, it must be remembered that even a short time ago this type of research with portable equipment, able to be operated in-situ with respect to a work of art, was not possible. The four major techniques are XRF, Raman, FTIR, and Fiber Optic Reflectance Spectroscopy (FORS). A brief description of each follows.

X-ray Fluorescence Spectroscopy (XRF) XRF is an elemental spectroscopy, and the portable unit used extensively in the research for this dissertation is sensitive to the presence of elements with atomic number 13 to 88. The premise of the XRF technique is that an incident x-ray source is focused on a spot area of analysis where the beam interacts with the atoms on the surface of the sample. The energy provided by the beam causes one of the inner shell electrons to be ejected, and an electron from one of the atom's outer shells drops in to fill the hole. The positive difference in energy between the excited state and the final state of the atom results in the production of a photon, the fluorescence event. The instrument's detector captures the fluorescent photons and records their quantized energies, which directly correspond to the characteristic XRF lines for the particular element. A spectrum is then produced of the collected photons in counts versus energy (keV).

Particular characteristics of x-ray physics cause this type of analysis to be significantly non-trivial when it comes to the analysis of artists materials. The efficiency of producing a fluorescence event, and then of detecting it can vary depending on the instrument settings. This is in addition to the x-ray absorption cross-section inherent to the element (and thus material) itself. Then several scattering and attenuation effects can further complicate the resulting spectrum. The positive aspect is that the technique has existed for quite some time and, in principle, the physics is thought to be well understood. Many studies have been carried out on cultural heritage artifacts using XRF, in 2011, 115 are reported at the Denver X-ray Conference alone [19].

Because an XRF user on cultural heritage artifacts, both on the acquisition side, and the interpretation side, must have a certain level of expertise to apply the technique to the study of artifacts, it is all the more important to establish and follow a well-defined methodology. In addition, in order to expand the use to a wider range of users, this technique should have clearly stated guidelines and limitations. Some progress has already been made with regards to this [19], but there is still a ways to go [20].

Raman Spectroscopy Raman spectroscopy has been mentioned as the ideal technique for identifying pigments [21] due to its unique specificity. Since most pigments are of mineral base, theoretically they have well defined Raman peaks and produce spectra that can be easily matched to database entries. Only a few pigments are not

Raman active. However, Raman spectroscopy has not seen wide adoption for several reasons. Historically, one reason was because the technique had not yet been adapted for portable use. This has changed in the last few years, though portable systems can also suffer from pollution of the signal from ambient light, thus becoming ineffective in field scenarios where the working conditions cannot be completely controlled.

The other reasons are due to the fact that the Raman spectra are often compromised with signal to noise issues. Typically organic materials produce a fluorescence that can often overwhelm the spectrum and obscure the relevant pigment peaks. Since painted materials are inherently a complex mixture of organic and inorganic components this makes analysis consistently trickier, and feasibility for good results then needs to be determined on a case-by-case basis. Some areas of research where Raman spectroscopy has shown particular promise are in the identification of dyes on illuminated manuscripts and printing blocks [21, 22].

Presently Raman spectroscopy is seeing more application through surface enhance Raman spectroscopy (SERS). Novel hydrogels are being incorporated with silver nanoparticles to enhance the Raman effect. These gels can be safely used non-destructively on some works of art to effectively reduce the signal to noise issue making Raman a viable technique again [23, 22].

Fiber Optic Reflectance Spectroscopy (FORS) The concept behind FORS has inspired the current innovations in Imaging Spectroscopy (IS). FORS is essentially traditional UV-VIS-NIR spectroscopy applied with a fiber optic cable (with a built in light source) operating in reflectance mode, making it portable and easy to use. The downside to FORS is the fact that it is a spot analysis, and that it is not absolutely specific to pigments. Because it is an optical technique, FORS is measurably influenced by the paint mixture and it is not possible to de-convolute the resulting curve for semi-quantitative analysis. Thus, only qualitative evaluations of the data are possible. FORS is nevertheless useful for its non-invasive and portable qualities, and databases of FORS spectra [24] form the basis for considerations in the chemical imaging methodology developed in this dissertation.

2.2.2 Analysis of Microsamples

Microsamples can provide information that is not able to be determined from other non-invasive methods [25]. It is for this reason that they have been an acceptable part of conservation practice since the early years of conservation science, especially when this information is required to plan a critical intervention. There are too many techniques shown in the right column of figure 2.7 to cover all of them in this sub-section, therefore, a more general review will be presented instead.

A microsample is a small paint chip taken from the painting. It can be procured with an x-acto knife, and it is usually difficult to see with the naked eye. As mentioned previously, the aesthetic impact on the painting should be minimized when sampling. They are usually taken adjacent to losses, on the sides of the canvas, or in other inconspicuous locations. The sample should include all layers of the painting from the surface to the ground layer, and should be taken in a way that the stratigraphy of the layers remains intact. A procured sample is then visualized under a compound microscope (see Microscopy, section 2.3.1). Microsamples are usually less than one millimeter in size, and the thickness can measure between 100-500um.

The analytical technique used will determine whether the sample is embedded in a polystyrene resin. Synchrotron techniques like micro beam XRD, XRF, 3D tomography, and PIXE prefer samples that have not been embedded (or are embedded and then microtomed to achieve a thin section). Attenuated Total Reflection (ATR) FTIR also prefers a sample that has not yet been embedded. Post-embed techniques include:

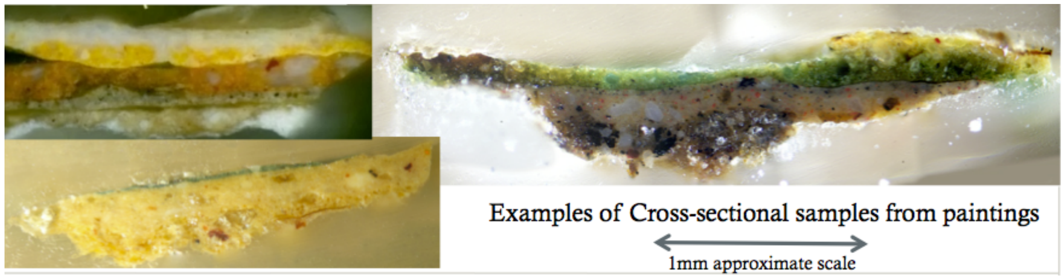

Figure 2.8. Three examples of cross-sectional paint samples, showing the variability in layering and grain size. [1]

microscopy, micro-Raman spectroscopy, SEM-EDS, and micro-FTIR analysis. For these techniques, a polymer resin (usually polyester or polystyrene), which sets at room temperature and does not require heating to set, is prepared in a mold. Molds are filled halfway up and pre-set, then the sample orientation is confirmed by viewing under the microscope, the sample is inserted using forceps, and the mold is filled with polymer. Once the embedded samples have finished setting, they are polished to the ideal depth for viewing the stratigraphy of the painted layers using successively finer polishing meshes. Careful attention must be exercised during the polishing phase as to not over polish, and this is accomplished by frequent pauses for viewing under the microscope.

The most common technique of analysis for embedded samples is SEM-EDS, which is carried out quite frequently due to the straightforward nature of the technique, its reliability, and suitability for obtaining useful information. The advantage of SEM-EDS over the non-invasive pXRF is the spot size, the ability to hone in on a particular layer within the stratigraphy and make a pigment identification. It is also useful to examine visually the morphology of the mineral crystallites making up the pigment, where individual granules can be selected for analysis by EDX.

Materials analysis techniques that will not be addressed in this dissertation but deserve a mention, are those that require a sample and proceed to destroy or consume the sample to make the analysis. These include HPLC, GC-MS, LA-ICP-MS, and

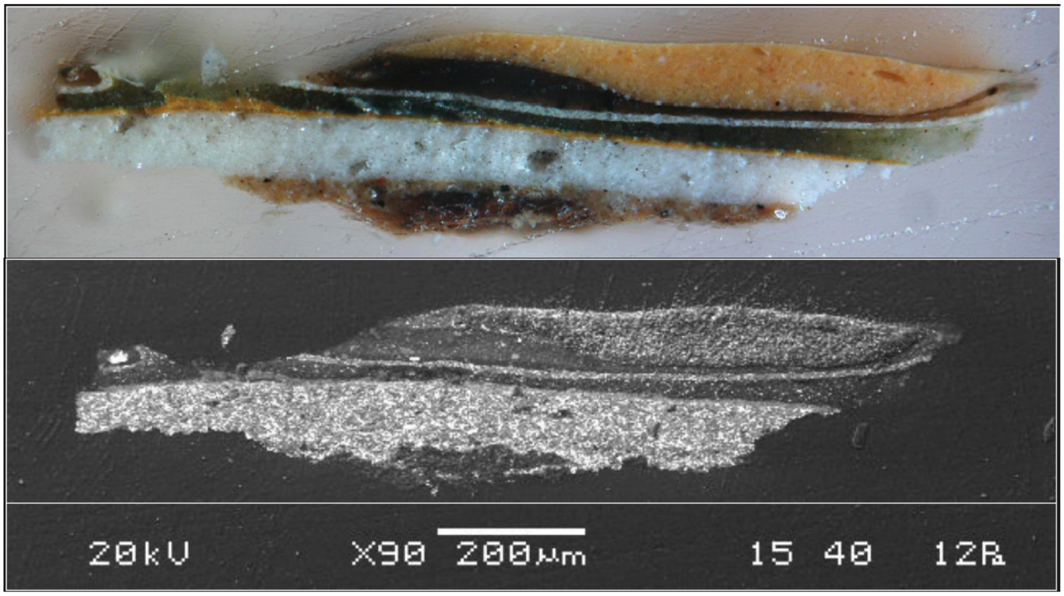

Figure 2.9. Example of a cross-sectional sample embedded in resin. Top: visible light, Bottom: SEM back-scattered electron imaging. [1]

carbon dating. Each has its own place and utility within the research field. The mass-spectroscopy techniques are mostly geared towards the identification of binding media, ICPMS can be used to evaluate the ratio of isotopes of specific elements of interest (such as Pb), and carbon dating is often useful in provenance or authentication cases. It can be said that these are impractical techniques for a routine diagnostic evaluation, though the mass-spectrometric tools are a standard way to determine the varnish material.

2.3 Image-based Documentation and Diagnostics

Imaging is undoubtedly a fundamental component of a documentation plan for cultural artifacts because it provides a visual record of the state of conservation. Nowadays, it is likely the first way an artifact is digitally recorded, and perhaps the most frequent way in which the digital record is updated over time. Traditionally, we think of imaging in the form of digital photography in the visible region of the spectrum, however, this chapter will work to expand the view of the reader to include other common diagnostic imaging exams that are used in the evaluation of cultural artifacts. Diagnostic imaging describes techniques that result in datasets that are visual in nature and typically capture the objects response to light in different regions of the electromagnetic spectrum. They can be captured on film, or as is more prevalent now, by digital sensors.

Some of the imaging techniques discussed in this chapter, due mostly to their digital nature, can provide semi-quantitative datasets from the meta-data associated to the values of each pixel of the composite image. In this way, statistical techniques like principle components analysis (PCA) can offer more information into the meaning and interpretation of the results, providing an especially useful way to measure statistical significance and variance within a dataset [12].

Lastly, imaging techniques are especially important because they produce data that has a spatial component directly associated to the artifact being examined. When a multi-technique approach is being used to assess the materials present in a work of art, it must be designed so that the datasets can be precisely overlaid for comparison. This is an important consideration for the methodological design of the diagnostic exam for pigment identification, and will be discussed further in Chapters 3 and 5.

2.3.1 Microscopy

Microscopy is often an overlooked tool in the diagnostician's box. It should, instead, be the routine first pass for a look at the painting. While striving for absolute objectivity, scientists may underestimate the ability of their own eyes to see the painting, however conservation scientists know that this is the essential first step. After a thorough look with the naked eye, an objective microscope should be used to survey the painting. Features that may be illuminated include, the exact nature of the craquelure, which may have been painted on for effect, or which may be filled with varnish from a restoration treatment, or may not be present in some places. Also important is the layering structure.

Often not able to be confirmed without a sample, sometimes layers may be seen by viewing through the microscope, for instance, if a brushstroke hasnt completely covered the previous layer, or if the paint is somewhat transparent when magnified, or in the case where there is flaking paint or losses. Next, the quality and type of brushstrokes, to a trained eye, it might even be possible to identify the type of brush used. Lastly, any incising or texturing should become apparent under the microscope.

It is recommended to spend several hours intimately getting to know the painting by viewing under the microscope. This will reveal where it is possible to take samples, and what information those samples might contain. It will also give key insight into the likely possibilities for the paint layers, especially order of execution. All of this preliminary information can prove useful when interpreting the imaging diagnostics and analytical exams, including XRF spectra, and therefore detailed notes should be kept to retain the observations.

If sampling is considered to be an option, it should be carried out only after the routine non-invasive diagnostic exams are carried out. At minimum technical photography (section 2.3.2) should be undertaken, and if at all possible, an x-ray radiograph and preliminary XRF point analysis should be taken. These datasets should be thoroughly analyzed before sampling. Then, when the samples have been collected, they should be visualized under the microscope, and visible and UV fluorescence images should be captured. Photography is carried out after the sample has been embedded so that a cross sectional, planar view is obtained allowing for optimum focus. Additionally, the sample should be viewed under crossed polarized light, since this provokes a characteristic response in certain mineral pigments.

2.3.2 Technical Photography (TP)

Technical photography (TP) is now the accepted term for the type of diagnostic imaging often called multispectral imaging in the past [7]. Multispectral now connotes that the spectral resolution be below a certain threshold, widely accepted to be between 10-50nm. Instead, technical photography is indicative of an imaging method utilizing multiple bands, or regions of the spectrum; yet, it also goes beyond that definition because it includes modes like false-color infrared and raking light. Thus, the community has settled upon the suitable term technical photography, which is used here.

Figure 2.10 shows a thumbnail representation of the technical photography imaging modalities (it also includes x-ray radiography, which is instead treated as a separate technique, see section 2.3.4). The diagram shows that different wavelengths have varying

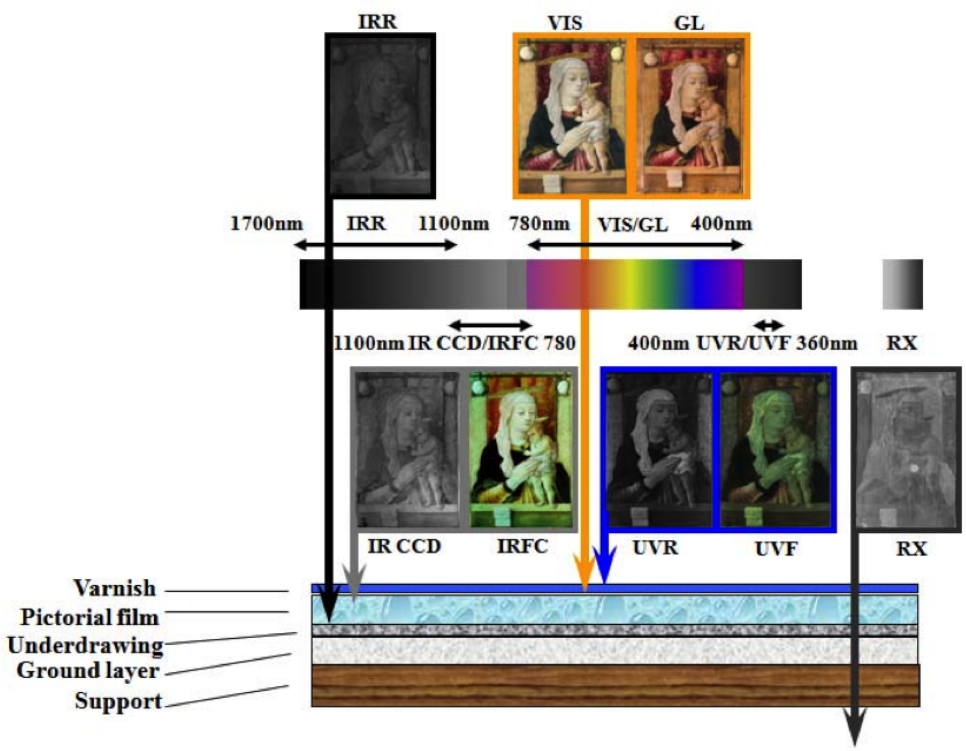

Figure 2.10. Imaging modalities of technical photography and their relative stratigraphic sensitivities.

ability to penetrate the layers of the painting. Most painted materials become transparent somewhere in the infrared region of the spectrum, and thus the IR reflectogram can reveal the underdrawing of the painting, executed in IR absorbent charcoal. Imaging data from the pigments checker and FORS data on individual pigments can help to determine their transmission in the infrared, though this can be affected by mixtures, layering, and binding media. Since paintings are meant to be viewed with the human eye, reflectance values are high in the visible regime. The wavelength reflected determines the color, though not all colors that appear similar visibly have the same reflectance profile, this is where the infrared false color technique can help to distinguish between pigments. The ultraviolet imaging modalities are particularly surface sensitive, especially if the painting is varnished or glazed. The UVF mode captures ultraviolet induced visible fluorescence, which changes with the degree of crosslinking of the polymeric oils, and thus can be used to detect areas of retouching (old and new varnish). Lastly, the raking or grazing light technique illuminates the painting at a small angle (with respect to the surface), and the shadows produced are captured as signs of topographic detail. Raking light is probably best seen with the naked eye, and perhaps one of the most difficult images to capture in detail with the typical technical photography setup due to the angles and lighting scenario.

Cultural Heritage Science Open Source, a scholarly reference for low-cost technical expertise, has published several articles detailing the instrumentation and methods of TP, and unless mentioned otherwise, the methods in this dissertation are congruous with the information contained in the references by Cosentino.

A short summary from a methodological standpoint is that technical photography is the logical next step to follow after viewing the painting by eye, and then under the microscope. The imaging modes provide key materials information, and the amount of detail able to be achieved is tunable according to the diagnostic scenario (see also Chapter

4.2). The panoramic method demonstrates a significant user-experience improvement due to the automation of the camera mount, and the ability of common software packages to reconstruct spherical panoramas [15].

The Pigments Checker

The pigments checker is a reference developed by Antonino Cosentino and Cultural Heritage Science Open Source. It consists of swatches of 54 historical pigments laid in gum Arabic on a lignin and coating-free paper. The paper is not treated with optical brighteners, is not UV-fluorescent, and it reflects infrared light. Two cross-hair lines are printed on each swatch of paper before the application of paint, in order to have a means to evaluate the pigment transparency. The Pigments Checker becomes a handy reference tool for the conservation scientist employing the methods of low-cost technical photography for imaging diagnostics. Calibrated images are available open-source on the web [24] in six imaging modalities. The AIC PhD target is incorporated into the checker as an additional standard [11]. To carry out scientific examination with the intent to produce semi-quantitative results, requires the use of a standard. Usually, NIST or ASTM can provide a suitable calibration or reference standard, but in the case of artists' pigments over the centuries the vast nature of materials used, as complex and potentially inhomogeneous mixtures makes this impossible. The pigments checker is still a simple solution, but it has been reliably prepared from a set of traceable pigments offered by the manufacturer Kremer. Thus, it makes an applicable and appropriately accessible reference for use in imaging diagnostics.

2.3.3 Multispectral and Hyperspectral Imaging

The terms multispectral imaging and hyperspectral imaging are already beginning to be replaced with the new player to the game, imaging spectroscopy. Multispectral

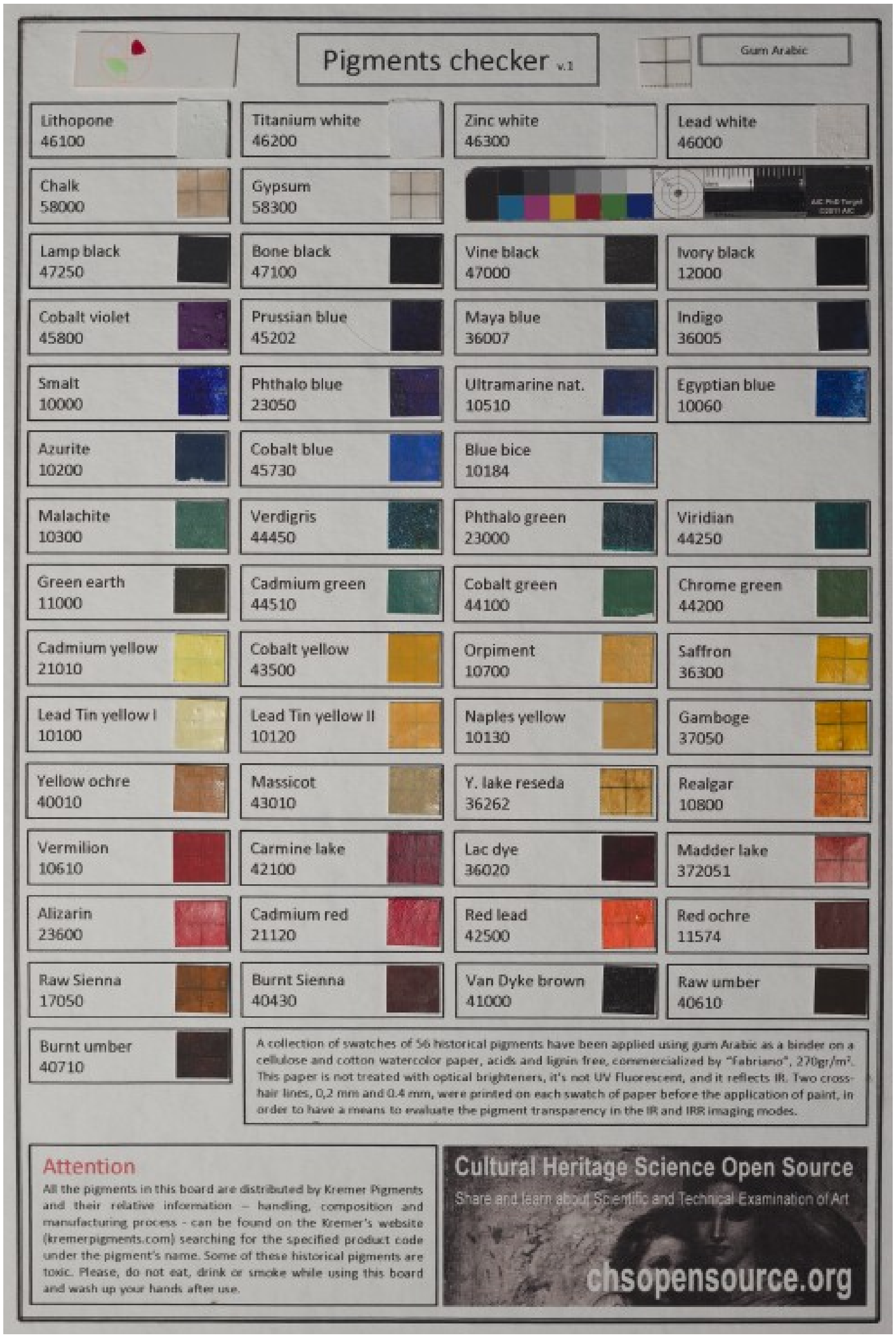

Figure 2.11. The Pigments Checker developed by Cultural Heritage Science Open Source (visible light).

came into use to describe diagnostic imaging instrumentation capable of parsing the UV-VIS-NIR region (approx. 300-1100nm) into wavebands 20-50nm wide, suggesting 20-30 images making up the entire region. Hyperspectral started to be used when the spectral resolution improved to less than 10nm bandwidth, with state of the art systems practically achieving a width of 4nm at present. With this type of resolution, chemical and molecular features are more recognizable even within the complex materials scenario of painted surfaces. For this reason this imaging technique has evolved to be called imaging spectroscopy, for the fact that the data resembles spectra collected with FORS or by FTIR, but is shown as a 3D data cube, where the 2D image is extended over the spectral range. Sophisticated systems using advanced sensor technologies originally developed for military use can cover the range 200-2500nm at 4nm resolution [16].

Multispectral and hyperspectral imaging have been applied to the study of dyes and lakes [26], of pigments on manuscripts [27], in mural paintings [28], as well as in paintings, and of chromophores in glassy objects. The main advantage is to apply reflectance spectroscopy in-situ over large areas to study materials in a non-invasive way. The image cubes produced in these prominent multidisciplinary investigations possess a wealth of information that a multi-technique approach is required to interpret. HSI is remarkable in the specificity by which it can identify markers that connect to a pigment or binder identification [16] especially when coupled with PCA to determine spectral end-members. However, it is also limited by the optical properties of the painted layers, in the penetrating capability of the illumination source within the medium, and thus the content of sub-surface material information (for example, the composition of the ground layer).

Given that very few institutions are capable of building the system previously noted as state-of-the-art, and the technologies involved would be cost prohibitive for adoption on a large scale, opportunity to carry out multispectral imaging or hyperspectral imaging is not viable for the large majority of stakeholders and conservators. In these cases, MSI and HSI are usually substituted by TP, however, a low-cost multispectral setup has recently been demonstrated by Cosentino [15].

2.3.4 X-ray Radiography and Neutron Activation Imaging

Although X-ray radiography and neutron activation imaging are valuable material sensitive diagnostic imaging methods in their own right, they are not considered practical for a standardized methodology seeking wide adoption in conservation practice. Yet, this seems paradoxical because the x-ray exam is in fact used prevalently in the museum world, and many museums have a dedicated facility for taking x-radiographs of their objects, including paintings.

Elements and materials have an x-ray absorption factor, and can be more or less radio-opaque. As we know from the lead shields that often are used to protect the operator and/or patient, lead is a good x-ray absorber and is thus highly radiopaque. That makes the use of lead white fairly easy to visualize on an x-ray, as it appears bright in the image. In addition to interacting with the painted layer, x-rays pass through the object as a whole. The film (or digital detector) is placed behind the object with respect to the source rays, and as such a projection image is captured after the rays have interacted with the sample. In this sense, all the layers, including the support are superimposed in the resulting image. X-rays can provide information on structural integrity, revealing concealed cracks or wormholes, and whether a treatment has been applied, such as filling with gesso, or securing with nails. One of the more exciting results of an x-radiograph is when a painting underneath a painting is revealed, as happens rather frequently since artists had reused canvasses to save money on supplies. Section 2.3.5.2 will provide a more detailed example of investigating paintings under other paintings.

X-radiography cannot be used to characteristically identify pigments, but it is an important technique to reveal otherwise hidden stylistic elements, like brushstrokes, fingerprints, and previous works, if they have been made with materials that exhibit contrast due to their radio opacity. Producing a good image that allows for these interpretations to be read depends on that material nature of each artifact individually, and a safe space is required for analysis. Digital detectors are still not available at an attainable price point for most, and the film procedure adds another layer of complexity when it comes to the development process. It must also be mentioned that interpreting or reading an x-radiograph is not a straightforward procedure. While we know very well the anatomy of a human being, the ability to read and interpret an x-radiograph (obtained by practice) is not a common skill, notwithstanding the fact that the irradiation time, maximum energy, current, and development procedure can produce vastly different images of the same artifact. [29] X-radiography should be considered an informative and powerful tool requiring a dedicated specialist to perform and interpret. Thus, it does not fit the characteristics for a pragmatic and routine diagnostic approach for the chemical imaging of paintings.

Neutron activation analysis (NAA) was actively explored as an elementally sensitive imaging method in the 1970's primarily by researchers at the Metropolitan Museum of Art in New York. An appendix of the Science of Paintings text is devoted to a technical recap of NAA on the utility of the method and the general way in which the exams are performed [2]. The authors admit that there are few publications after this initial popularity, but dont speculate as to why that is. Some reasons that may be offered are: it involves using ionizing radiation (a neutron source), and the safety and infrastructure allowances that go along with that; it is only sensitive to a select few elements; paintings with cobalt in them should not be analyzed since the timescale of this decay is on the order of years. However, NAA is useful due to the penetrating nature of the radiation, and the allowable escape depth of the beta particles. It can be the best way to visualize the underlying paint layers in some scenarios. Although, Taft and Mayer mention that it's a pity the popular pigment lead white can not be imaged due to the inactivity of Pb with the method, this can be a positive trait of the exam when the overabundance of lead has obscured the x-radiograph making it difficult to read. NAA can produce clear elemental maps of the painted layers for the entirety of the painting's stratigraphy. Like x-radiography it must be deemed outside the scope of this chemical imaging methodology due to equipment, cost, safety, and accessibility requirements [2].

2.3.5 Chemical Imaging

Chemical imaging is a term heretofore applied sporadically in the cultural heritage diagnostics literature to describe techniques from Tof-SIMS to MA-FTIR. It has been adopted for the purposes of this dissertation to generally describe methods of analysis that provide chemical information and represent that information in a way that is visually connected to an image of the artwork. This can be through diagnostic imaging, or by a mapping form of analytical diagnostics, or indeed, by a computerized digital image highlighting tool or automated image segmentation. The key factor is that the spatial domain and visual appearance of the artifact is connected to the chemical information being represented. These requirements will considerably enhance the reading and interpretation of the datasets and provide an accurate record to increase the repeatability of the exams (compared to when they are applied individually in a multi-technique approach). The chemical imaging methodology developed in this dissertation holds repeatability paramount, because it is a crucial step to allow for the time-monitoring (by tracking the results of the exam over and over through the record in the DCC) of state of conservation using these techniques.

Laboratory Techniques

John K. Delaney at the National Gallery of Art in Washington, D.C. has built a formidable hyperspectral imaging instrument, widely accepted as state-of-the-art for imaging paintings. The precision scanning apparatus is fixed to the wall of the imaging room and is arranged to move the painting, while the sources, sensors and optics remain fixed on an optical table. [16]

Isolated from the constraints put upon portable equipment and kept away from potentially wear inducing field scenarios, the level of detail able to be realistically achieved is higher in the laboratory, though the capability to analyze the work of art in-situ is limited to practically moveable works. In the effort to accommodate all painted works of art, the methodology in this dissertation is intentionally designed to be portable.

Portable: Scanning Macro XRF (MA-XRF)

Scanning Macro XRF came onto the research scene as a sophisticated rendering of a mainstream technique capable of generating elemental maps, and especially notable for achieving subsurface pictorial information (ie. imagery of paintings underneath known paintings) [30]. Indeed it is agreed that this tool provides a very attractive complementary technique to the imaging diagnostics suite of exams. The issues arise when considering its practicality. In fact, this is to be expected from a technique only developed very recently (2011). However, there do exist some fundamental limitations to the technique that will detract widespread user adoption.

According to the literature, MA-XRF is best utilized to map primary elements of pigments, as no examples of trace element imaging are shown. [31] This is in accordance with the time constraints posed by acquisition. There must be a trade off between the spot size of the instrument (the pixel resolution of the resulting image), the collection time required to obtain a sufficient amount of signal, and the area able to be covered. In order to decrease the collection time and make mapping larger paintings accessible, a signal processing approach has been applied to extract the signal from the noise for individual spectra. The method is not faithfully described in full detail in the existing literature, representing a main encumbrance to repeatability and adoption of the technique by other users. Additionally, the software programs necessary to handle the resulting data are still in the development stage.

Chapter 3

Design of the Diagnostic Exam

3.1 Design Criteria and Building Blocks

This chapter will serve to describe the features of the exam methodology while elaborating on how they serve to meet the ideal design. Two common analytical tools frequently applied in the field of cultural heritage diagnostics, TP and XRF, have been chosen for the diagnostic exam.

Technical photography is a streamlined version of multispectral imaging, where wavebands in different regions of the electromagnetic spectrum are captured in digital image form. It was selected for the visual nature of the technique, the ability to access material characteristics related to pigment and color, and the ability to be carried out with low-cost equipment [4]. The technique has been well documented and there are also many resources already available to the research community [32].

X-ray fluorescence spectroscopy is a non-invasive tool, which provides point-based elemental information about the materials present in the spot of analysis. XRF is a desirable technique for this type of exam because the instrumentation is versatile. The portable XRF (pXRF) instrument used in this dissertation can easily travel to field sites and operate without need for external power supply. The portable XRF has the disadvantage of a larger spot size, however, its ease of operation, agility, and relatively accessible price point make for reasonable trade-offs. The marriage of TP and XRF in a synergistic way has been previously demonstrated [33, 6].

The procedure for data collection is described in Section 3.2.2 and efficiency is prioritized, so that the time spent by the operator to acquire the data is minimized. After the data have been collected, additional tools for qualitative data evaluation and processing are proposed. For TP the recommendations generally follow the AIC guide [11] and the work of Cosentino [6]. For XRF, the data treatment procedure was custom designed to fit the purpose of the exam – to accurately identify the artist's palette of pigments. To achieve a method that would not be brand specific, the use of proprietary software was avoided. Some new tools on the market, in addition to open source software, help to make this achievable.

Finally, recommendations for data storage and retention of important metadata will be presented, and the user experience will be discussed.

3.1.1 Field Work Scenario

Anywhere outside of a traditional laboratory environment with fixed instrumentation, reliable access to power sources, bench tops and fume hoods is considered a field scenario for the purpose of this dissertation, though this notion generally applies in the discipline as whole. Most often, a trip to a museum to visit the artifact in question is considered going out in the field. TP and pXRF are ideally suited towards work in the field, as is demonstrated through the case studies in Chapter 4. A method that can accommodate the field scenario will ultimately experience higher adoption rates, and thus these factors were prioritized.

3.2 Exam Workflow: A Guide Manual

The exam workflow should comprehensively cover the procedures for data acquisition, processing, interpretation and storage. Since traditionally the details have been found all across the literature and presented in many different contexts, this section will serve as a guide to co-locate all of the steps specifically tailored to the purposes and desired outcomes of the diagnostic exam.

3.2.1 Data Acquisition

Technical Photography The exam begins with TP documentation. The most common approach is to use a modified digital camera where the in-built IR filter has been removed [6, 34]. This is the sensor with the lowest upfront cost. The TP method doesn't specify a specific experimental setup, but instead a series of wavebands that are collected using a suite of filters. The data in this dissertation have been collected following Cosentino [4, 35]. Of course, other setups can be employed and the brand of the camera and the lens is up to the user (see recommendations [24]). A simple upgrade is described in [7] using a monochromatic sensor where typical RGB and false-color images can then be recomposed. Most often, one single shot will not provide the level of detail sufficient to document the state of conservation of the painting, and therefore many shots are taken and then tiled in mosaic fashion [36]. Through the case study described in Chapter 5.1, it was discovered that a panoramic method [36] can work better than a planar method depending on the size of the artwork.

When the TP analysis is set up, the focal length of the lens must be balanced with the standoff distance from the work of art to arrive at an appropriate image size. The level of detail is important because too much detail can easily turn into a waste of effort, as a proportional amount of new information is unlikely to be obtained. Image stitching, or mosaicking, is often a computationally intensive task. Based on experience with all of the steps of the methodology, the appropriate level of detail depends on the features present in the work of art and the level of detail that must be captured. For paintings exhibiting small cracks, care should be taken to be able to adequately visualize this important conservation factor. The best way to confirm that there is sufficient resolution for the purposes of the piece of art is to view a test shot at 100 percent on the monitor. The test shot will confirm the focus and for most lenses the auto-focus feature of the lens can be used. A pixel size of 50um, meaning that 20 pixels cover 1mm, is suggested as a maximum limit, even in artifacts possessing a high level of detail. This limit is imposed also to keep the stitched images from becoming too large and unwieldy to be manipulated and viewed on the computer. The TP modalities were summarized in Section 2.3.2, however only IR, VIS, UVR, and IRFC are implemented in the diagnostic exam. Infrared reflectography from 1100-1700nm can be captured with an InGaAs camera, however this sensor has a much higher price point and cannot be considered low-cost. Additionally, the UVF technique is difficult to achieve optimal lighting conditions and cannot be well standardized, and thus was also omitted.

X-ray Fluorescence Spectroscopy The XRF survey is carried out after a careful analysis of the TP images. The practitioner looks for regions of the work displaying different characteristics of absorbance and reflectance in the various wavebands of light (UV-VIS-IR). One approach demonstrated is to follow a flowchart as in 3.2. To characterize the palette, areas appearing each color visibly must be analyzed. In addition, the TP images are reviewed to check if there is different behavior in other wavebands for regions that appear the same color visibly (most notable difference in the IRFC image). At least a few points of each color in the palette should be selected for analysis. This usually results in around 20 to 30 points analyzed per painting, and the exam takes a couple of hours. Several spectra should also be collected in various areas on the support, ideally areas devoid of pigment materials. A detail image of the location of analysis is recorded, along with an accurate spot size reference and the instrument settings as annotations so that a map may be created. A digital tablet platform to help the practitioner manage the imaging and analytical diagnostic datasets is described in Section 5.2.

The instrument used in this dissertation was the Bruker Tracer III-SD, which features user selectable settings for the beam voltage and current. The “lab-rat” mode using 40keV and 14uA was chosen to maintain the ability to recognize characteristic K-lines of higher weight metal elements such as Cd and Sn (appearing at 23 and 26keV respectively and needing to be excited above those energies). No filter was used and the path was in air. These basic settings can likely be replicated or emulated on other portable or fixed XRF units.

Since the palette of pigments used by the artist would have been finite, it follows that the number of points analyzed by XRF to identify the palette can also be finite. The main advantage of the method is the combination of spatial and point based datasets and the informed selection of points, which allows the user to operate quickly and obtain sufficient information at the same time. Further studies will look to validate pigment distribution and compare segmentation based on the imaging and spectroscopic datasets, both together and separately.

3.2.2 Data Storage and Post-processing

A data management pipeline that can take in the data and repeat the processing steps in the same way for each set of images and spectra has been envisioned. The research group at CISA3 has started to construct such a data pipeline during the research project for the WAVEcam application described in Section 4.1. Here the steps will be summarized and the design will be explained.

An external hard drive or server with a minimum storage level of 1Tb is necessary for the initial storage of the data from one work of art. Once the dataset has been processed into the final TP images, in theory the source image data will no longer need to be stored. This will decrease server requirements for the permanent record of the digital clinical chart. The XRF spectra represent small file sizes, less than a few megabytes in total. It is recommended that a small flash drive with the contents of the DCC be kept physically with the artwork, and that an additional copy be kept on another server, or ideally with a cloud storage provider. Of course, the necessary precautions for security, privacy, and copyright must be followed as well.

The mosaic images must be stitched to form the final image. This can be accomplished with a few available software programs [32]. The UVR and IR images must be changed to grayscale from RGB (if using a DSLR with Bayer filter for the sensor instead of monochrome). To compose the IRFC image the visible and IR modalities must be combined and the RGB channel components shifted. This is performed by overlaying the IR image on top of the visible one, setting the transparency to 50 percent and setting the RGB channels to IR:(Red - R100, Green All 0, Blue All 0) and visible:(Red All 0, Green - R100, Blue - G100). Alignment can be achieved more easily if the visible and IR shots were taken in exactly in the same position. The images can then be stored in a multilayered TIFF file containing all the TP wavebands overlaid on top of one another for ease of comparison.

To obtain a qualitative sense of the elemental makeup of the support (ie. the matrix of the material under the layers of paint), spectra are acquired in several points on unpainted areas. The matrix spectra are then averaged and the resulting spectrum provides a reference for the user to discern peaks, which perhaps do not correspond to the pigment layer, but instead to the support underneath. A simple subtraction is then performed, taking out the contribution of the support material from the spectrum of

Pigment	VIS	UVR	UVF	IR	IRR	IRFC	XRF major element 1	XRF minor element 2
Lead white	White	Bright	blue	Bright	Same	white	Pb	
Titanium white	White	Dark	none	Bright	Same	white	Ti	
Lithopone	White	Bright	yellow	Bright	Same	white	Ba	Zn
Gypsum	White	Bright	white	Bright	Same	white	Ca	S
Chalk / Calcite	White	Dark	white	Bright	Same	white	Ca	
Cobalt Violet	Blue	Bright	none	Dark	Same	green	Co	As, P
Prussian Blue	Blue	Dark	none	Dark	Same	black	Fe	
Maya Blue	Blue	Dark	none	Bright	Same	red	organic (none)	Si
Indigo	Blue	Dark	none	Bright	Same	red	organic (none)	
Smalt	Blue	Bright	blue	Bright	Darker t	red	Co	Si
Phthalo Blue	Blue	Dark	none	Bright	Same	red	organic (none)	
Ultramarine (nat.)	Blue	Dark	none	Dark	Same	red	Si	Al
Egyptian Blue	Blue	Dark	none	Dark	Same	red	Cu	Si
Azurite	Blue	Dark	none	Dark	Same	purple	Cu	
Cobalt Blue	Blue	Bright	blue	Bright	Darker t	red	Co	
Blue Bice	Blue	Dark	none	Dark	Same	blue	Cu	Ca
Cadmium Yellow	Yellow	Dark	red	Bright, a	Same	white	Cd	
Cobalt Yellow	Yellow	Dark	none	Bright, a	Same	yellow	Co	K
Orpiment	Yellow	Dark	none	Bright	Same	yellow	As	S
Saffron	Yellow	Dark	yellow	Bright, a	Same	yellow	organic (none)	
Lead Tin Yellow I	Yellow	Dark	none	Bright, a	Same	yellow	Pb	Sn
Lead Tin Yellow II	Yellow	Dark	none	Bright, a	Same	yellow	Pb	Sn, Si
Naples Yellow	Yellow	Dark	none	Dark	Same	yellow	Pb	Sb
Gamboge	Yellow	Dark	none	Bright, a	Same	yellow	organic (none)	
Yellow Ochre	Yellow	Dark	none	Bright	Same	yellow	Fe	K
Massicot	Yellow	Dark	none	Dark	Same	yellow	Pb	
Yellow Lake Reseda	Yellow	Dark	yellow	Bright	Same	yellow	organic (none)	
Realgar	Red	Dark	none	Bright	Same	yellow	As	S
Carmine Lake	Red	Dark	none	Bright	Same	orange	organic (none)	
Madder Lake	Red	Dark	red	Bright	Same	orange	organic (none)	
Alizarin	Red	Dark	none	Bright	Same	yellow	organic (none)	
Cadmium Red	Red	Dark	none	Bright	Same	yellow	Cd	
Red Lead	Red	Dark	none	Bright	Same	yellow	Pb	
Red Ochre	Red	Dark	none	Dark	Same	brown	Fe	
Vermilion	Red	Dark	none	Bright	Same	yellow	Hg	S
Malachite	Green	Dark	none	Dark	Same	blue	Cu	
Verdigris	Green	Dark	none	Dark	Same	purple	Cu	
Phthalo Green	Green	Dark	none	Bright	Same	red	Cl	Cu
Viridian	Green	Bright	none	Bright	Same	red	Cr	
Green Earth	Green	Dark	none	Dark	Same	black	Fe	K
Cadmium Green	Green	Dark	none	Bright	Same	pink	Cd	
Cobalt Green	Green	Dark	none	Bright	Darker t	pink	Co	
Chrome Green	Green	Dark	none	Bright	Same	red	Cr	Pb

Figure 3.1. Screen capture of the spreadsheet used to collect TP data for each pigment on the Pigments Checker.

the pigments. Elements with characteristic lines with positive levels of counts are then attributed to the paint mixture. All spectra are saved as .TXT files. The tallest peaks after the subtraction will be named as major elemental components, and the remaining elements will be listed as minor, secondary, or trace components. The results of imaging and XRF for each point analyzed are put through a series of flowcharts tracking the detectable characteristic pigment response to the analytical technique.

3.2.3 Data Interpretation

The data interpretation phase has been structured for eventual implementation into a searchable "smart" database. The first spreadsheet (Fig. 3.1) is a container for the TP imaging response to the pigments in the pigments checker.

The information in the table should be compared with the results of the data to identify the pigment through processes of deduction and elimination. It is possible that the spot analyzed will be a mixture of more than one pigment, however, this does not pose a major problem since the objective of the exam is to determine the artist's palette. The information from several spectra of the same color, taken in different locations will help to decrease the effect of mixed pigments from obscuring the primary coloring component.

When searching the database, the user must simply enter in the response of the colored area in each of the TP modalities, then for the XRF analysis select from a list of elements - which is the major peak, and what is the secondary peak, if there is one. The database then implements a decision tree following the flowchart specifically designed from the data table. First an approach to begin with the elements and arrive at the pigments was outlined, (Fig. 3.2), to assess the differentiating capacity. Then, improved flowcharts were created by appending the XRF response onto the TP flowcharts stemming from visual color as the first identifier.

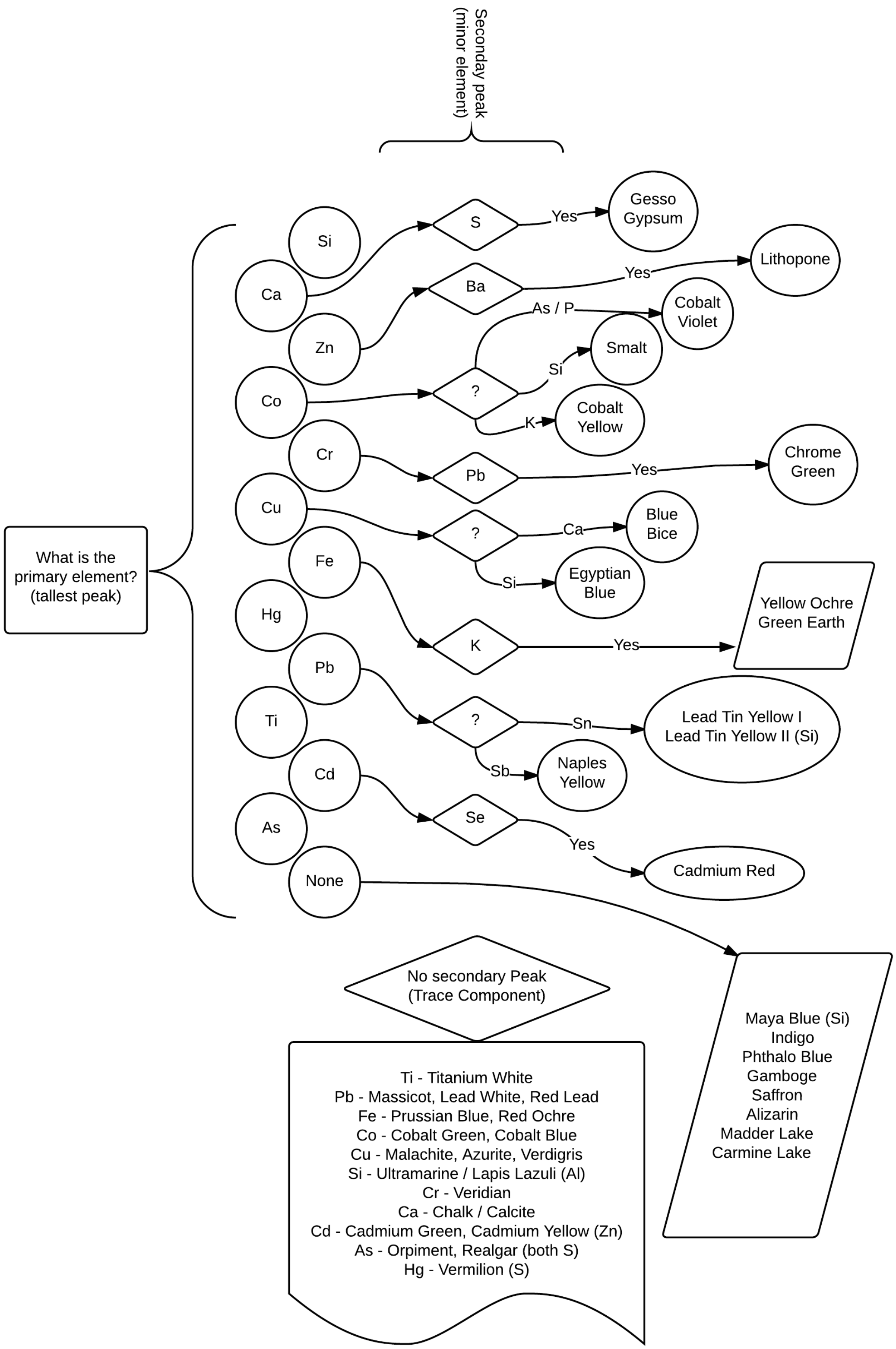

Figure 3.2. Flowchart to narrow down pigment options based on primary and secondary peaks (elemental composition) of the XRF spectrum.

3.3 An Improved Flowchart Method

A flowchart method for the identification of pigments by multispectral imaging was described by Cosentino [4]. However, what the paper actually presents is a flowchart method following technical photography (as large wavebands are taken in fluorescence and reflectance modes). The diagnostic exam for pigment identification will adapt and build upon this flowchart method. Some imaging modalities are omitted due to their inaccessibility (UVF and IRR) and XRF point-based spectroscopy is added. The synergy of the two techniques results in an improved reliability and differentiation of pigments, while economizing the general diagnostic approach.

It is always logical to start with the visible color of the pigments on the surface of the painting, both when considering the technical photography images and when interpreting the results of XRF analysis, so the flowcharts naturally begin here. Figures below reproduce the flowcharts in [4] with the addition of XRF results. For TP, only the VIS, UVR, IR, and IRFC imaging modalities were used because the acquisition environment and equipment can easily affect UVF and IRF (IRR was deemed too expensive).

Summary The improved flowchart method effectively narrows down the field of ambiguous pigments able to be positively identified by either of the techniques alone. It has been streamlined based on visible color of the surface pigment to follow decision trees based on the observable pigment characteristics using the exam protocol. Out of the group of roughly 50 pigments used in the pigments checker (black pigments were not included in the study since they are usually organic and do not produce any characteristic response with either TP or XRF), 20 are theoretically not able to be distinguished from their similar counterparts with XRF alone, and 16 are not able to be distinguished with

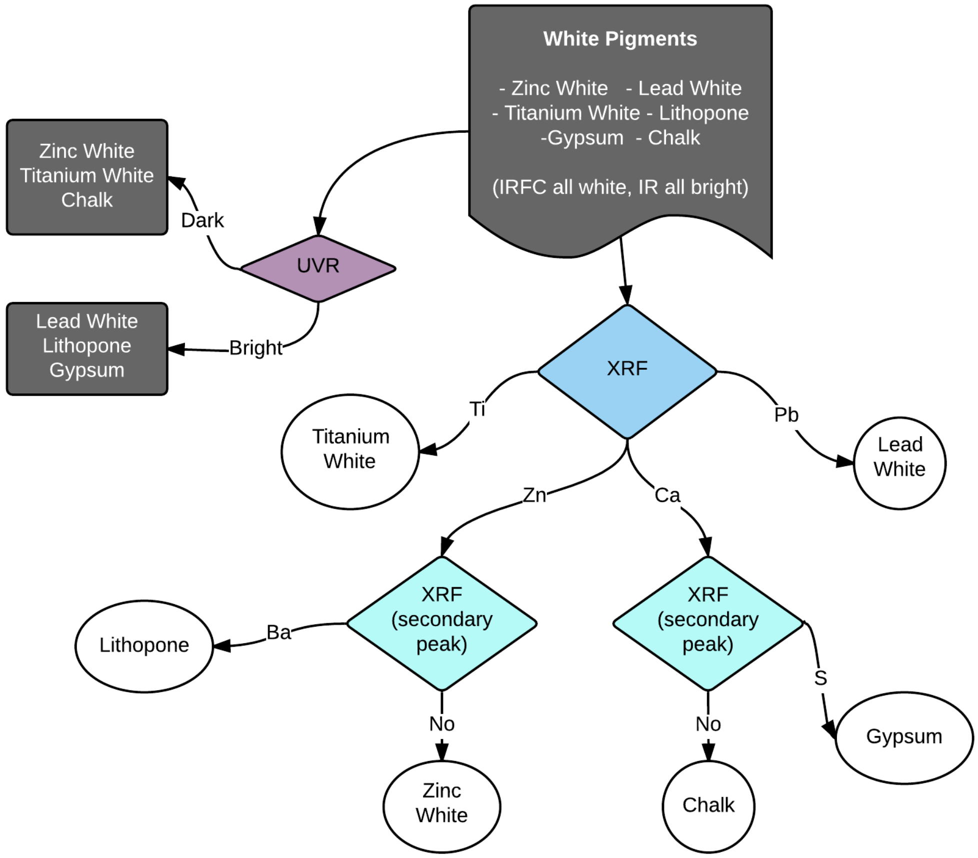

Figure 3.3. Flowchart for the differentiation of white pigments using the diagnostic exam methodology.

the full TP suite. By applying the dual-technique protocol the field of indistinguishable pigments is cut in half to only eight pigments, most of which are the organic dyes and colorants not well adapted to detection by these two techniques in particular. In some cases, just one other imaging modality, UV-fluorescence or IR-fluorescence would determine the pigment, however, these techniques are difficult to setup, calibrate, and detect in an automated way, they could instead be applied on a case-by-case basis.

Results There was a measurable overall improvement in the ability to narrow down a pigment assignment and define the artist's palette of pigments using the improved flowchart method. For clarity, comparisons have been made, not to the flowcharts in [4], but instead to abridged TP flowcharts which use only the 4 modalities chosen for the diagnostic exam.

For the selection of white pigments the camp of possibilities was narrowed from two groups of three pigments exhibiting a differentiating response to all six becoming identifiable (Fig. 3.3).

For the differentiation of red pigments the field was narrowed from seven left indistinguishable with imaging only to only two organic based lake pigments with the improved flowchart (Fig. 3.4).

In the case of green pigments the full TP method was able to differentiate all of the ones tested [4]. However, the reduced imaging suite left a group of three and a group of six to be unidentifiable. Adding XRF and using the improved flowchart (Fig. 3.5) regained the ability to distinguish all of the green pigments.

The blue pigments are some of the most difficult to separate using only non-invasive methods. In fact, the differentiation of these depend heavily on the ability to recognize a secondary element peak with XRF. This is because the response in the IRFC characterized as blue, black or purple, or red or pink, may be too similar to properly assign a positive identification. The XRF provides a necessary double check in this case and the camp is narrowed from about 7 pigments indistinguishable to only 2 organic ones, (Fig. 3.6).

For the yellow pigments, nine are left indistinguishable both with the first flowchart (Fig. 3.7) and with the reduced imaging set. The XRF helps by positively identifying the inorganic pigments, (Fig. 3.8). Only three organic pigments are left, one of which can be ruled out with UV fluorescence.

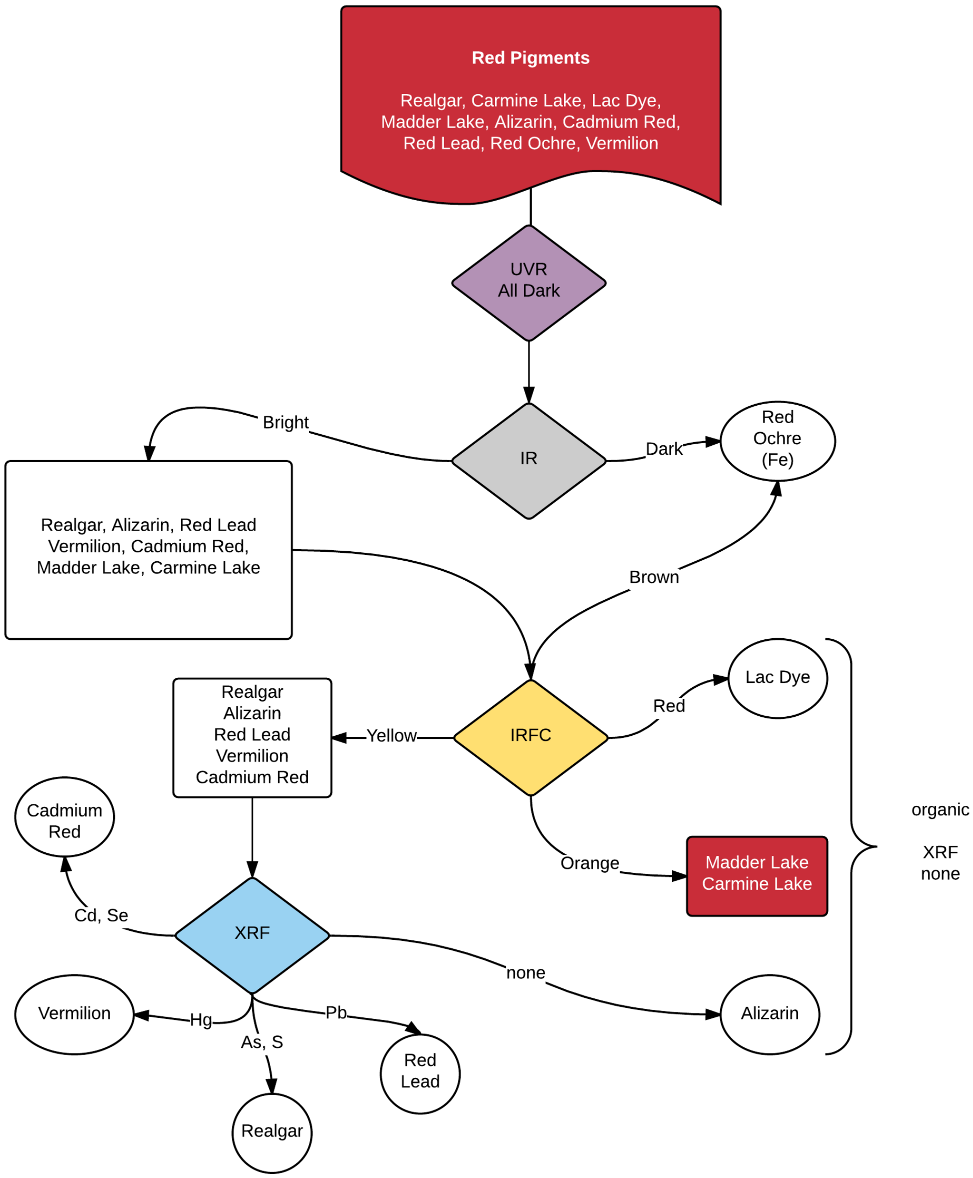

Figure 3.4. Flowchart for the differentiation of red pigments using the diagnostic exam methodology.

Conclusions The diagnostic exam architecture was designed to make use of flowcharts as a standardized way to follow the process of interpretation and decision making from the raw data to the final result. It forms a traceable path that can be checked at every turn for errors or misinterpretations. It is also readily able to be automated so that

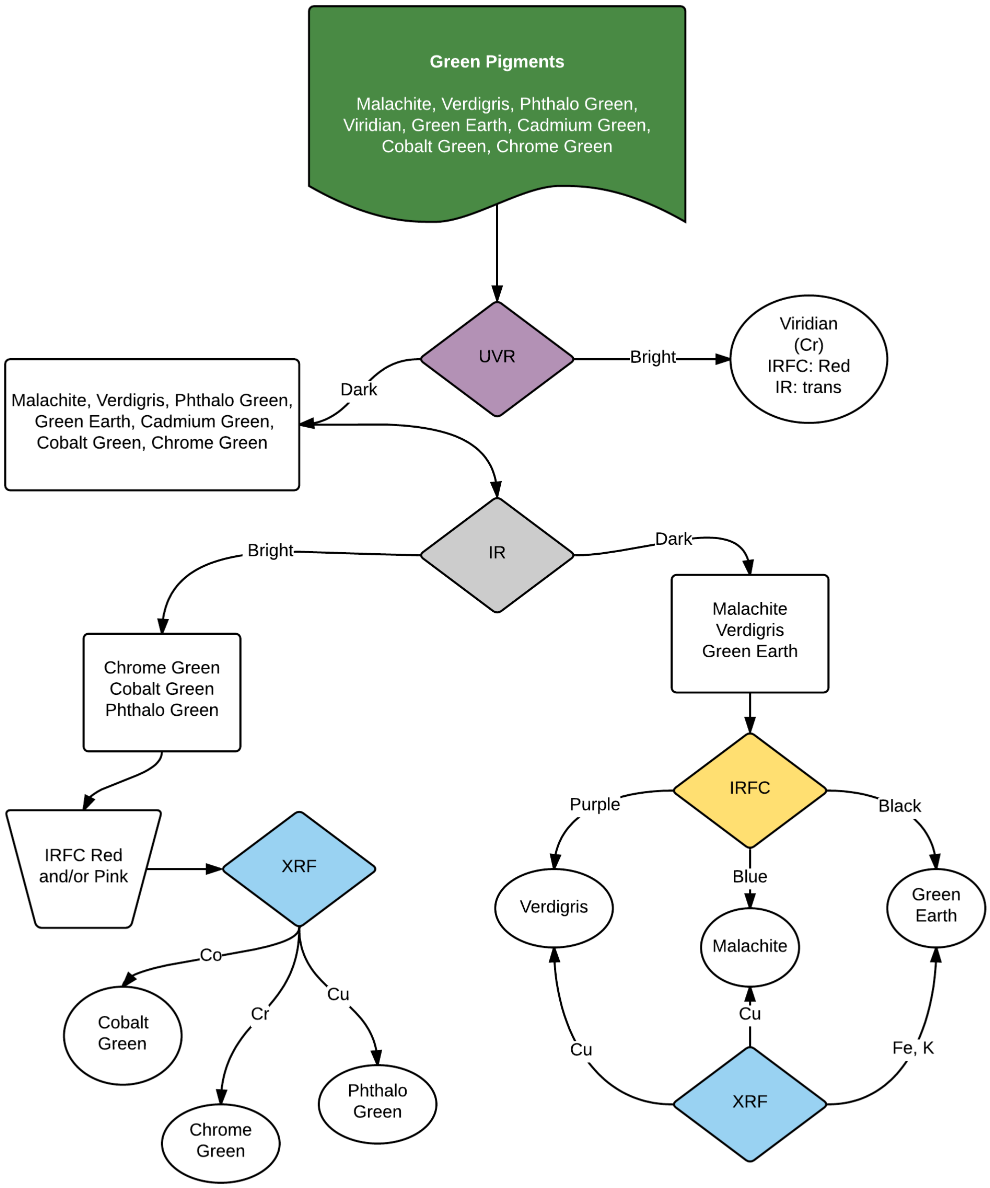

Figure 3.5. Flowchart for the differentiation of green pigments using the diagnostic exam methodology.

data can be batch processed in the background after they are entered into storage. The decrease in user committed time will enable higher throughput so that more paintings may be studied and "big-data" on artist's palettes may be objectively collected. The improved flowcharts are put to the test in some preliminary experiments in Chapter 6.

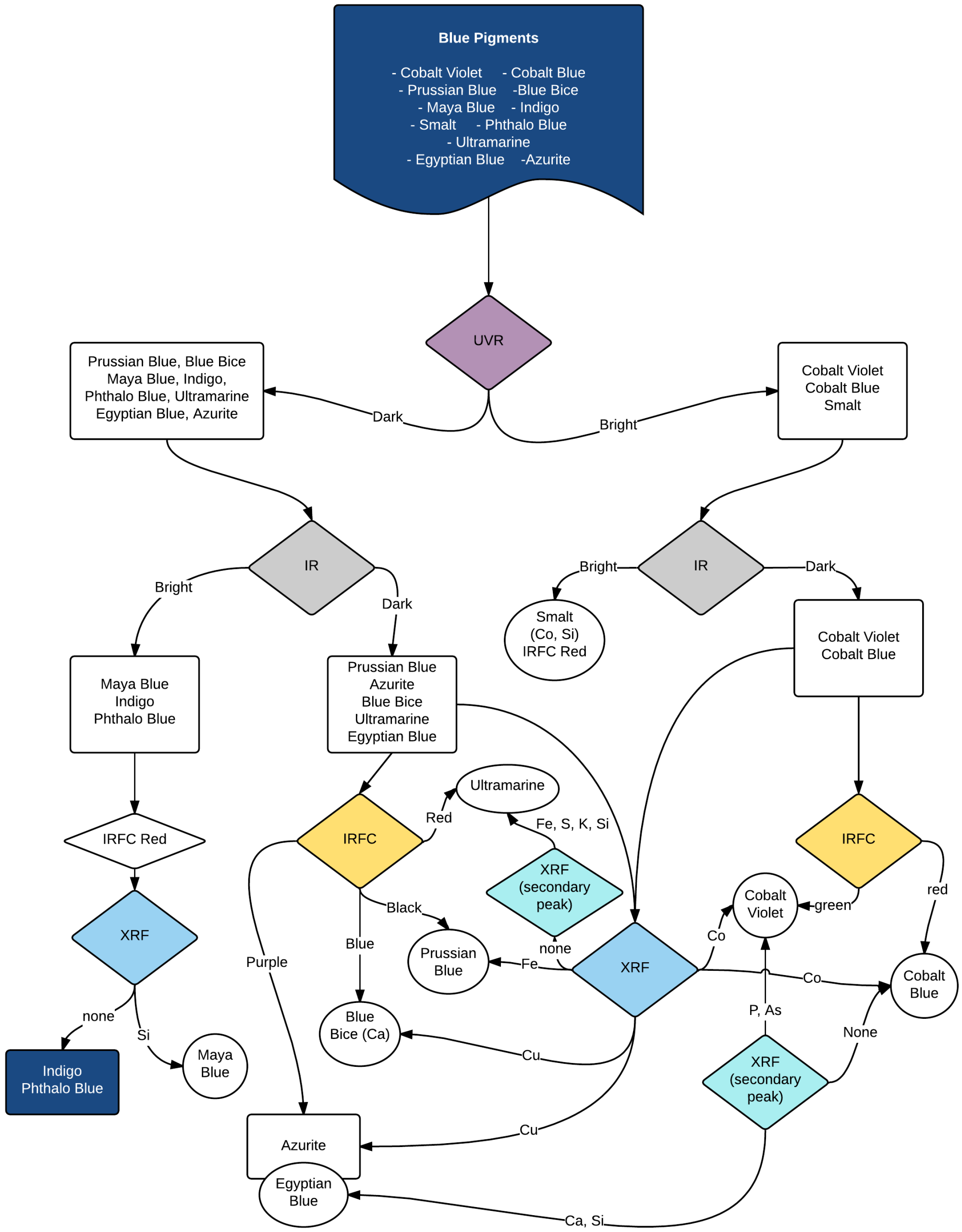

Figure 3.6. Flowchart for the differentiation of blue pigments using the diagnostic exam methodology

The material in Chapter 3 may be presented for publication at a later date.

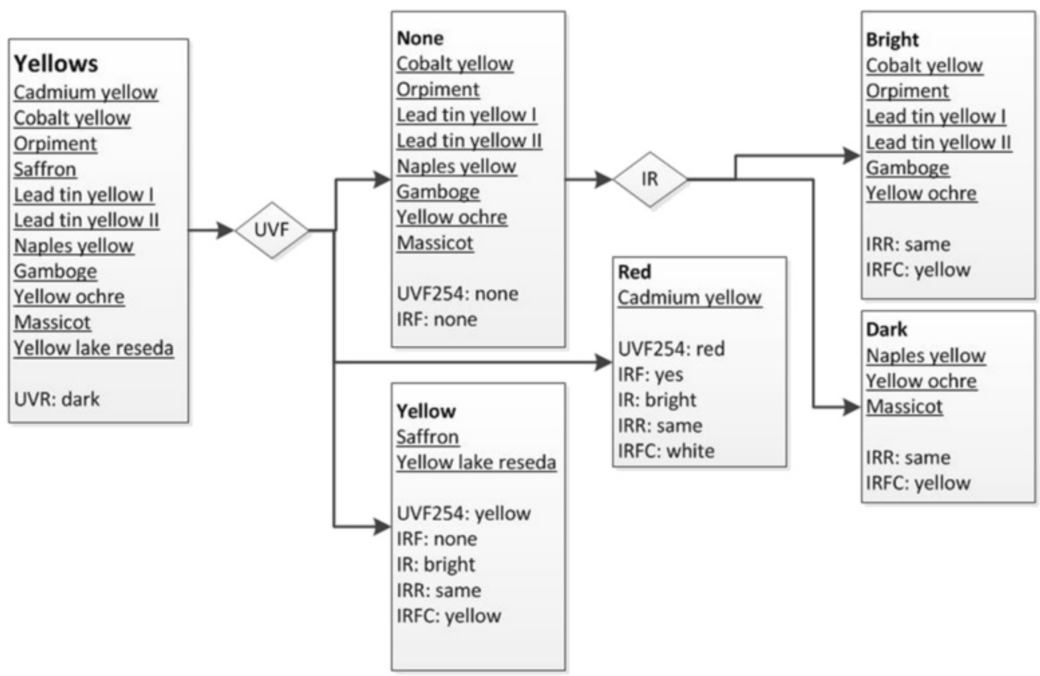

Figure 3.7. Flowchart for the differentiation of yellow pigments, from [4]

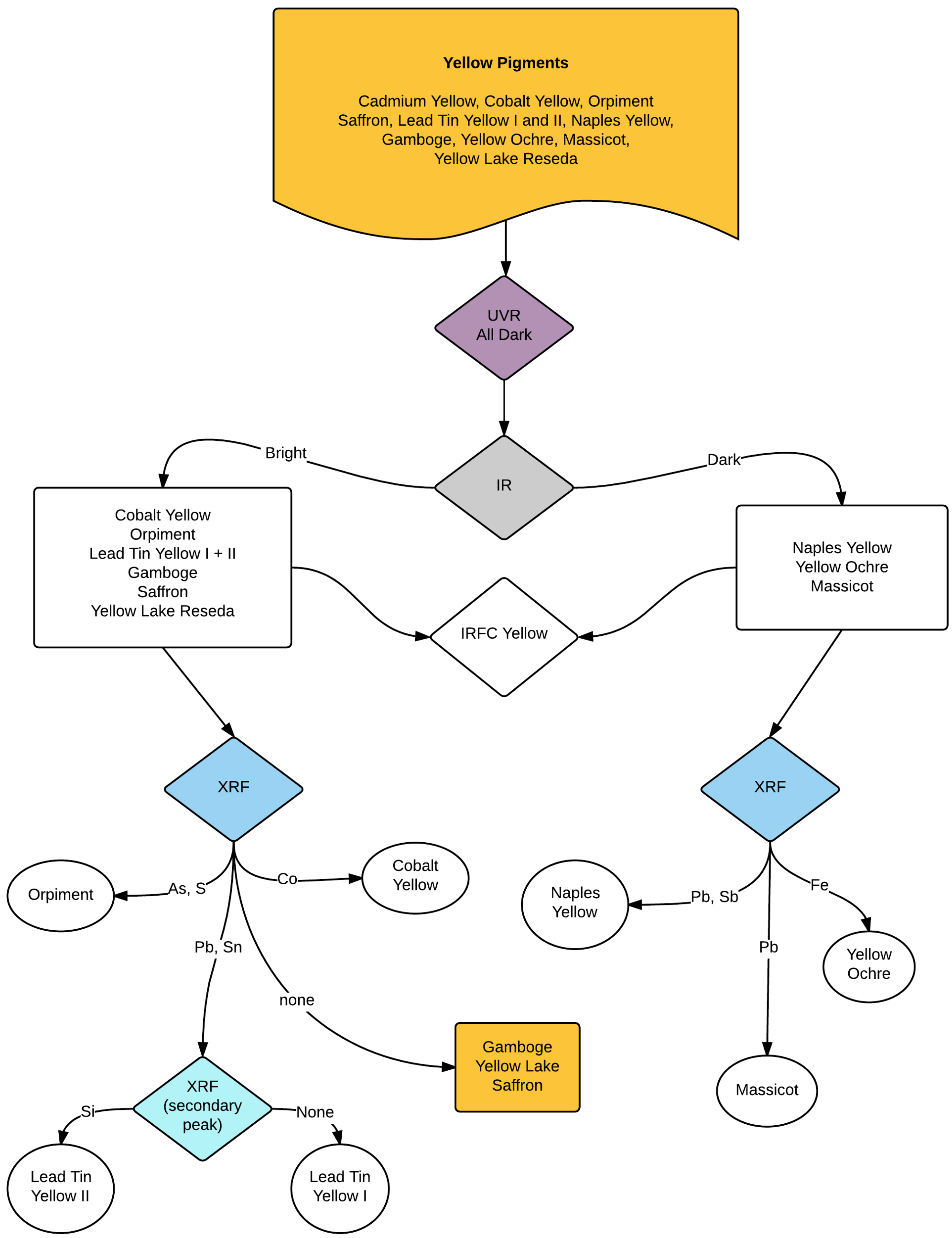

Figure 3.8. Flowchart for the differentiation of yellow pigments using the diagnostic exam methodology

Chapter 4

Field Applications - Case Studies Combining TP and XRF

The following case studies represent three different applications of these two techniques, on painted artifacts of three different typologies, where the techniques were used in conjunction in a way that is complementary from a diagnostic standpoint. All of these examples are from the work of the author and collaborating co-authors, and have been adapted to fit the narrative of this dissertation. The case studies were applications of the procedures in the diagnostic exam for non-invasive pigment identification, giving insight on how to formulate the methodology to address the defined goals while operating in a fieldwork scenario.

4.1 Historical Drawings: Leonardo da Vinci, The Adoration of the Magi

Leonardo da Vinci's "The Adoration of the Magi" drawing, held in the collections of the Gabinetto di Disegni e Stampe degli Uffizi, 436 E, Florence (Fig. 4.1); was studied with multispectral (multiband or TP) imaging, and the unique features identified were then investigated further with XRF. The diagnostic campaign allowed qualitative conclusions to be drawn about the artist's technique, and hypotheses to be developed

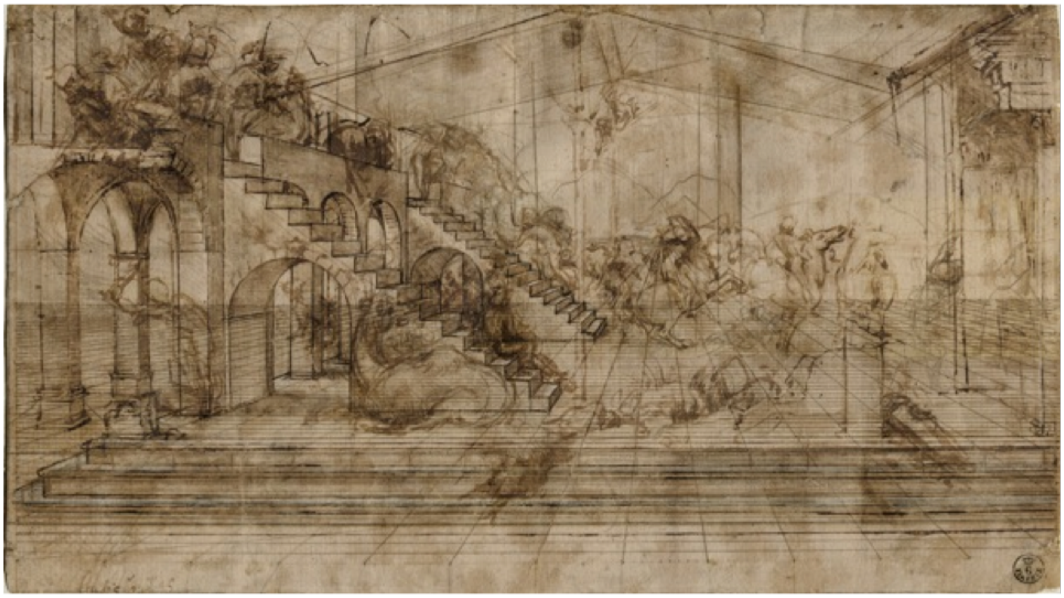

Figure 4.1. Perspective Study for the Adoration of the Magi, 1481, pen and iron gall ink, with silverpoint and ceruse on paper, 16.3 x 29 cm, Gabinetto Disegni e Stampe degli Uffizi, 436E, Florence.

about the materials used, the sequence of execution of various elements in the drawing, and the localization of areas which had been re-worked from the original state.

In this case study, the XRF analysis served as an important complementary technique and provided an objective confirmation that supported evidence from the diagnostic imaging analysis. The identification of the materials used, and the order and method with which they were applied, provided critical insight into the progression of design and motifs incorporated in the work by da Vinci. In addition, the intent to obtain valuable information for future conservation efforts was fulfilled.

X-ray Fluorescence (XRF) is now applied widely for investigations on artifacts of cultural heritage due to the presence of affordable, portable units that offer non-destructive, yet sensitive, elemental analysis [37].

These instruments, including the Assing Lithos 3000 used in this case study, can be easily transported to perform analyses in a museum setting or in the field, and may be

Figure 4.2. Leonardo, Adoration of the Magi, 1481. Charcoal and ceruse on gesso undercoat on wood panel, 243 x 246 cm, Galleria degli Uffizi, Florence.

set up to operate at close range without contacting the artifact.

This case study presents a method that combines multispectral imaging diagnostics with XRF point analysis in the study of a preparatory drawing by Leonardo da Vinci, as a way to make a comprehensive assessment of the entire artifact including the technique of the artist, the materials used, and the state of conservation of the artifact. An important point to address is that the method described here represents a relatively small investment in necessary equipment with respect to the wealth of information gained and to the time spent acquiring and interpreting the data.

Leonardo's Adoration of the Magi

The Augustinian monks of the Church of San Donato a Scopeto in Florence commissioned The Adoration of the Magi to Leonardo da Vinci, aged 29, in 1481 [38].

The drawing analyzed here was a study in preparation for the painting, its composition corresponding with approximately the upper third section of the large panel. This area contains both the focal point of the scene, as well as, the main architectural features of the work, while most of the figures are depicted below. The same methodology was previously used to study the panel painting; Seracini carried out those exams at the Uffizi Gallery in Florence in 2002, the results were what prompted the drawing to undergo this type of scientific analysis [38, 39]. The drawing measures a mere 16.3cm by 29cm, considerably smaller than that of the painting, indicating that there was no direct transfer from one to the other.

In addition to the non-traditional dimensions of the drawing, a watermark is absent from the parchment and there is visual evidence on the edges of the sheet that indicates it may have been cut down from a larger piece [38]. The drawing is held in the Prints and Drawings division of the Uffizi Gallery since it was recovered from the Medici collection around 1670. Out of the many studies Leonardo made for the piece, this drawing is one of two more significant works; the other is at the Louvre in Paris [38].

Methods and Instrumentation

The drawing was studied at close range with stereomicroscopy, raking (visible) light photography, black and white infrared imaging (1.1 to 1.7 microns wavelength), visible light, and ultraviolet fluorescence imaging. The entire array of multispectral imaging was carried out prior to choosing the points to be analyzed by XRF. The imaging diagnostics were completed using a DSLR camera with the infrared filter removed and CCD detector sensitive from 250-1100nm, and a near-IR camera with InGaAs detector sensitive to 1.7um. Images were taken at close range and then mosaicked to create a high-resolution digital file. For each spectral band range captured, the same pictures were taken to enable the composite images to be easily overlaid for cross-comparison.

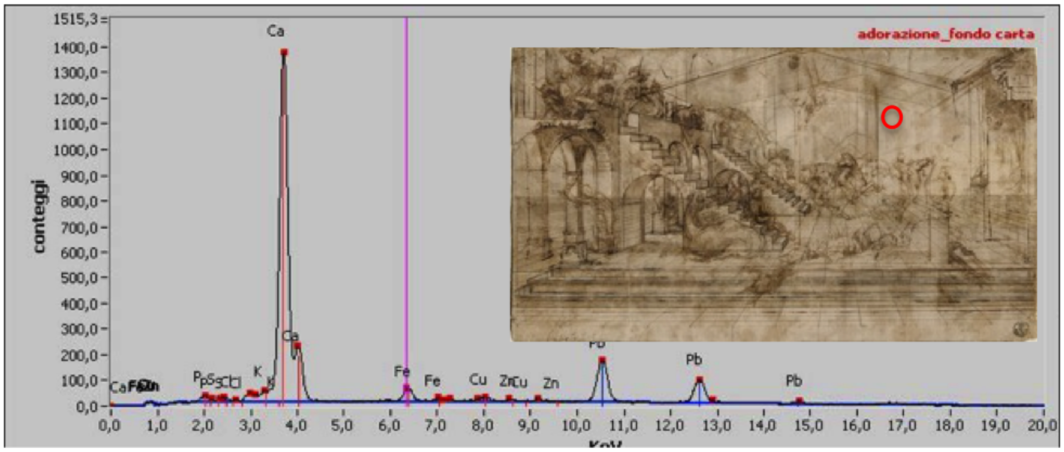

Figure 4.3. Drawing for the Adoration of the Magi: XRF spectrum of the paper, with area scanned shown.

The artifact was additionally studied under the stereomicroscope and inspected using raking light. The analysis resulting from the imaging diagnostics was able to inform the non-invasive chemical (elemental) analysis, carried out by portable XRF. Areas were chosen so that each type of material present would be included in such a fashion that cross-comparing spectra would potentially give more information than could be gained from each spectrum alone. XRF spectra were acquired with a portable instrument (Lithos 3000) designed and manufactured in Italy by Assing. The x-ray tube was equipped with a Mo target with maximum voltage of 30keV and current of .5 mA.

Materials Characterization

For XRF the matrix is always pertinent to the sensitivity and the semi-quantitative interpretation of the resulting spectra. In this case the x-rays completely penetrate and go through the paper, which is less than 1mm thick, and the spectra were acquired in ambient air (not with the aid of a vacuum pump). The paper was shown to contain Ca as the primary element with peaks also resulting from P, S, Cl, K, Fe, Cu, Zn, and Pb in lower amounts. These elements are commonly found in renaissance era papers due to the paper making process [40].

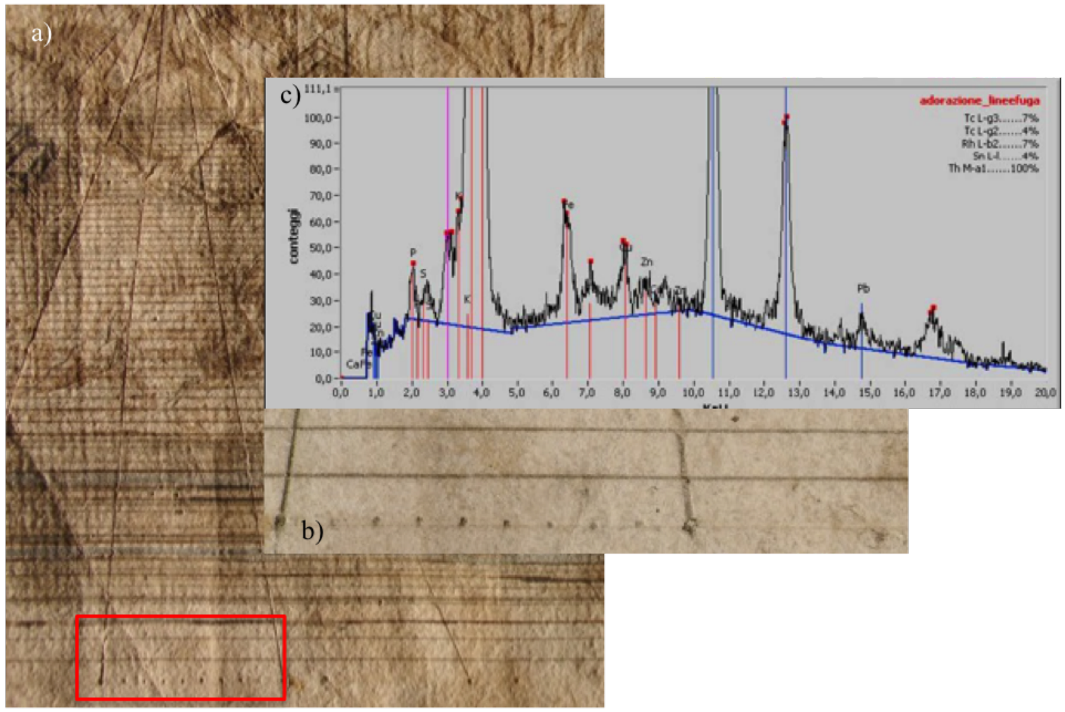

Figure 4.4. a) Raking light image, detail on perspective lines. b) Detail of the metal point where XRF analysis was performed. c) XRF spectrum of the metal point line.

The raking light image offers a detailed view of the texture of the paper where a precise perspective grid was laid out with an instrument that produced incisions. This tool was likely a form of metal point, which at the time would have been made from primarily Pb or Ag [41]. The grid lines follow toward the focal point, placed along the horizon line, dividing it into segments defined by the golden ratio. In this fashion, Leonardo followed the technique described in Euclid's Elements [38]. The golden ratio can be seen again in the Vetruvian man, and is a radical value that is also represented by the ratio of the length of a side of a regular pentagon to the length of its chord. XRF point analysis was performed on the perspective lines in the indicated section. It is difficult to tell whether the Ag-La line at 2.98eV is present because the Ar-K lines (from the ambient air) appear in the same region of the spectrum [42]. However, the Pb-L lines present are not observed to increase in magnitude when compared to those of blank paper, thus

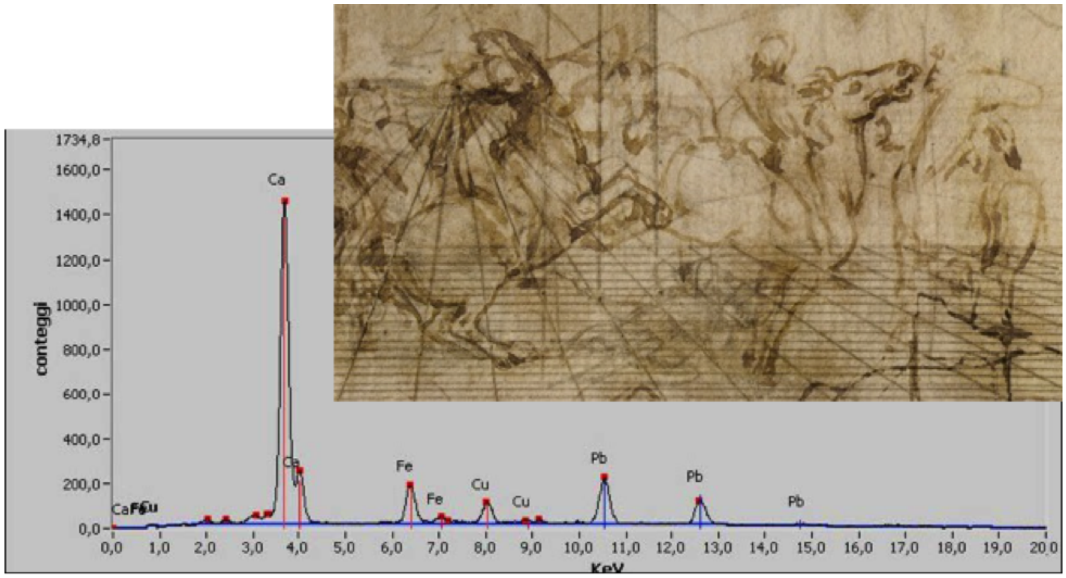

Figure 4.5. XRF spectrum of ink used in the figures.

contributing to [38, 41].

The precise perspective grid is what allowed for the nearly exact transfer of the architecture from the drawing to the painting. The infrared reflectogram of the painting reveals the underdrawing by the artist, which is a testament to this [38].

The figures in the drawing were carried out with Fe gall ink that was applied with a brush. In this case, XRF point analysis confirms this assumption by revealing elevated levels of Fe and Cu (when compared to the baseline of the paper matrix), which correspond to gall ink with made with Fe and Cu vitriol, typical of the time period [43]. Analysis of the artist's stroke with stereomicroscopy reveals that the ink was applied with a brush [38]. Some features of the architecture are highlighted with a white substance. XRF point analysis shows spectra exhibiting Pb-M lines, as well as, significantly elevated Pb-L lines, indicating that this is a form of lead white, likely $(PbCO_3)_2Pb(OH)_2$.

The state of conservation was assessed as a comprehensive evaluation of all the exams performed, but visually the image taken in transparency mode (visible light) speaks to the condition of the parchment. In the center portion there is a sizable tear, which

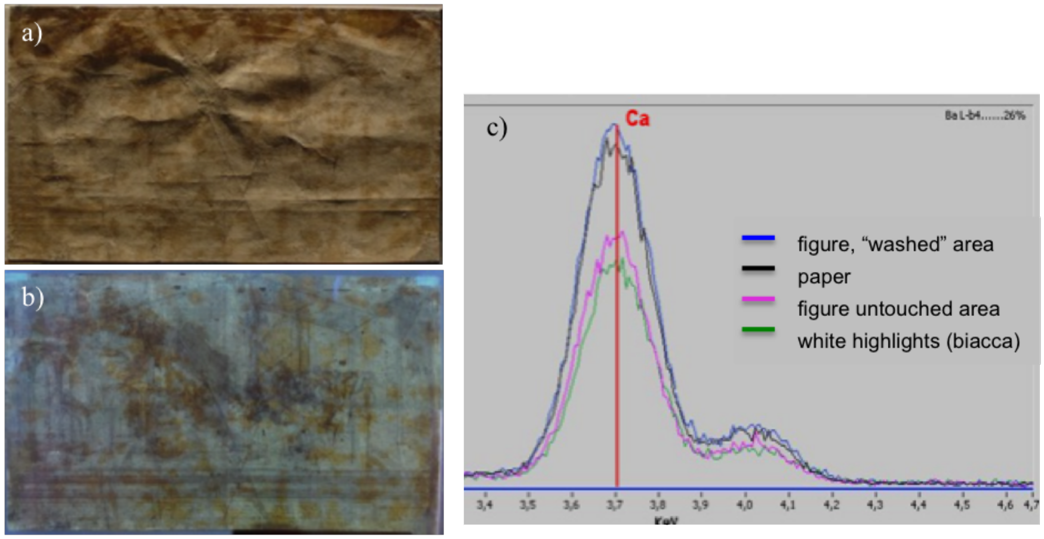

Figure 4.6. a) Visible image, verso. b) Ultraviolet fluorescence, verso. c) Ca Ka peak in XRF spectra.

has undergone repairs. There are also many small holes at the ends and intersections of the elements of architecture with the perspective grid, used to transfer the composition without recreating the entire grid, however there are no other holes. This is surprising because iron gall ink is known to oxidize over time and the corrosion tends to eat away at the paper [43]. No correlation was found between areas with Fe gall and deteriorated areas, indicating that this process has not occurred.

A pattern of discolorations is best observed on the verso of the parchment, and is apparent in both the visible and ultraviolet images. Organic matter commonly fluoresces in the visible region of the spectrum when irradiated with ultraviolet light, and imaging in UV fluorescence mode can show anomalous organic material in the artifact [40]. In these two images, it can be seen that the pattern of discolorations in the UV images matches that in the visible image. Four points were tested with XRF spectroscopy in an attempt to identify an elemental difference between the two areas. A marked difference in the level of Ca detected between a figure in the yellow-ish area and one in a blue-ish (UV image color) area, supports the theory that the blue-ish area has been "washed" with a

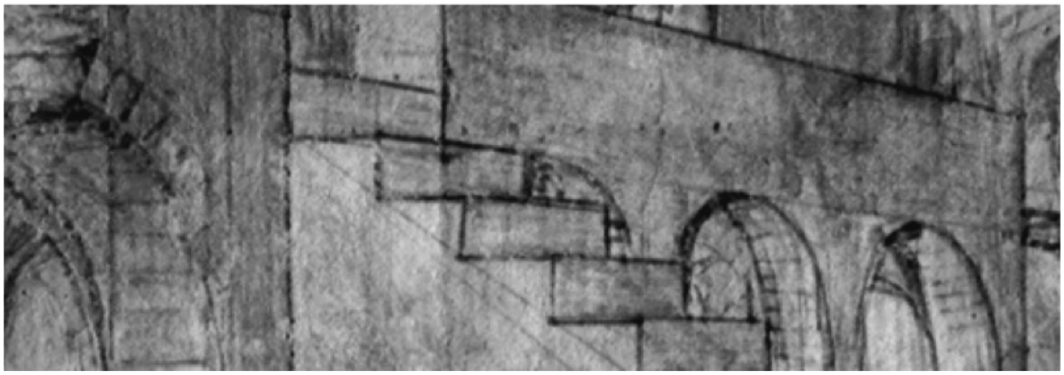

Figure 4.7. Infrared Reflectogram showing darkened areas, reinforced during a 19th century restoration.

calcite solution applied during a prior restoration. The organic binder in such a solution would display the blue fluorescence seen in the UV image, and this wash may explain why the iron gall ink exhibits little to no corrosion today. However, as seen by the uneven fluorescence pattern, the calcite wash was not applied uniformly to the entire work. In areas where we do see fluorescence, we can also see a darkening of some of the figures and architectural features. By comparing the UV, visible and IR images, it can be shown that these marks are not contemporary to the original sketch and were likely added during a 19th century "restoration" such forms of touch-ups and even extensive reworking being commonplace occurrence during that era [44].

Conclusions

With limited equipment and a requirement of non-destructive in-situ analysis, imaging diagnostics can be used as a powerful tool to inform XRF point analysis and provide critical information that will help in forming a comprehensive assessment of the technique, the materials used by the artist, and the state of conservation of the work. We have detailed the necessary equipment, analytical process, and interpretation of the results in the context of Leonardo da Vinci's study for the Adoration of the Magi. Combined with multispectral imaging, the portable x-ray fluorescence unit plays an important role in identifying elemental content to confirm visual interpretations and theories about the materials and the condition of the artifact.

4.1.1 Methodological Insights

The anecdotal descriptions in the above report contain key information obtained solely from the expertise of the researcher leading the study, in this case, Maurizio Seracini. It is important not to overlook the contribution of a trained eye to the interpretation of imaging diagnostic exams. This case study proves that the order of operations in the methodology is important and follows a logical progression designed through experience. The main point is that any point-based chemical analysis should only be carried out after the imaging assessment and careful and complete interpretation of the results, as was demonstrated here.

This procedure is very influential to the accuracy and detail of the reconstruction of artists technique and material history of the artifact, otherwise essential details are apt to be missed. This case was also fortunate to have been studied by scholars in the humanities, which proven by the copious references, greatly enhanced the narrative and understanding of the comprehensive evaluation. The conclusions determined that a rich and valuable dataset could be obtained with only two accessible, non-invasive diagnostic tools, which adds weight to the economy and efficiency of the underlying principles behind the chemical imaging methodology.

4.2 Frescos: Giorgio Vasari, The Battle of Marciano in Val di Chiana

The critical state of conservation of the Vasari fresco, “The Battle of Marciano in Val di Chiana” was assessed using imaging diagnostics and non-invasive chemical analysis. The comprehensive methodology detailed here enables the objective identification of the technique of the artist and the materials that were used. It also sheds light on prior restorative efforts and the extent of and the factors contributing to the decay of the fresco. The data compiled provides essential information in a report to local stakeholders tasked with developing a plan for the possible restoration of the fresco.

Historical Context Palazzo Vecchio is a medieval fortress that was built in the center of Florence in 1299. The Great Hall, called "Cronaca", was commissioned by Girolamo Savonarola and built in 1494 by Simone del Pollaiolo and Francesco di Domenico. Leonardo da Vinci was commissioned in 1504 to paint a mural for the Great Hall that would represent the victory of the Florentine Republic over the oligarchy of Milan on the plains of Anghiari in the 1440's. Between 1563 and 1574, after the Medici returned to power under Cosimo I, the architect and artist, Giorgio Vasari, carried out a complete renovation of the Hall. Vasari's work is what mainly defines how the Hall appears today (shown below).

The Search for the Battle of Anghiari Since 1975, Maurizio Seracini has been investigating the location and existence of "The Battle of Anghiari" painted by Leonardo da Vinci in the early 1500's . The mural was commissioned for an area 3 times that of the Last Supper, above the seats of the "Twelve Good Men" in the Hall of the 500. The mural has been lost ever since Vasari remodeled the Hall in the mid-16th century. It is believed to be hidden on another wall, behind the right fresco panel on the East wall, and protected by an air gap (between the two walls) intentionally left by Vasari. Seracini and his research team have demonstrated the existence of an air gap through radar scanning and endoscopic investigations. The research scaffold shown above was constructed for the most recent phase of the research, which was documented in a film produced by National Geographic.

Figure 4.8. Point cloud from LiDAR scanning visualized in custom software.

Millions of points representing the geometry of the Hall in 3D space were collected through LiDAR laser scanning of the Hall of the 500 in Palazzo Vecchio, Florence Italy. The 3D model reconstructs the Hall with centimeter precision. An accurate representation of the buildings architecture is the first step in the assessment of the state of conservation of the fresco.

The Battle of Anghiari research scaffold (Fig. 4.9) provided unique access at extreme proximity to the Vasari fresco, yet also made a significant area of the fresco inaccessible due to the support structure of the scaffolding. Here the exam methodology could be carried out on the pictorial surface of the fresco. The ability to overlay the multispectral images onto the three dimensional model of the room, wall, and surface topology extends the comprehensive nature of the investigations, and is currently being developed via a custom software built by co-author, Vid Petrovic.

Figure 4.9. Research scaffolding in Palazzo Vecchio's Hall of the 500, June 2012.

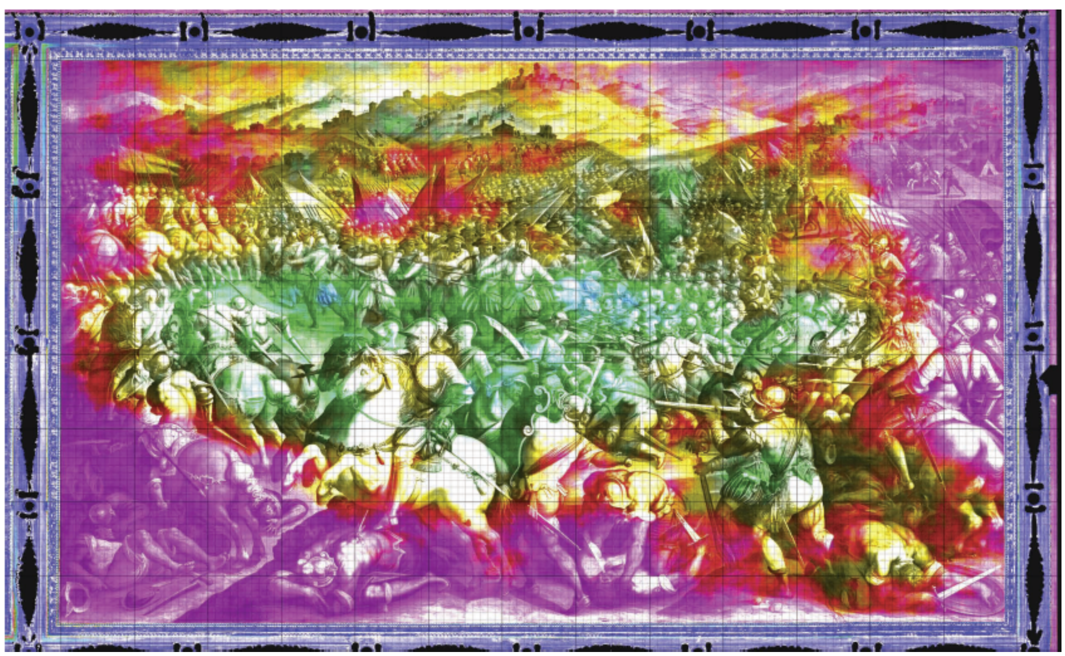

Figure 4.10. A topographical map showing distance from the viewer as color overlaid on the fresco design. Magenta areas are closer to the viewer and green/blue areas are farther away.

3D Modeling and Mapping Mural Topography Because a mural is a part of the architecture, a three dimensional model is extremely useful to capture the geometry of the artifact it its structural environment. In this case study a Leica Laser Scanner (LiDAR) was used to survey the Hall of the 500, resulting in a point cloud dataset that represented the architectural space. Two visual datasets were then extracted from the LiDAR point cloud, showing the topography of the fresco mural itself. This is an important way to assess physical deformation caused by detached plaster and determine areas subject to the risk of further deterioration.

Thermography Thermal imaging is based on the exchange of thermal energy (heat) between the structure and the environment. The contrast in the image is produced according to the properties of the materials constituting the structural support and plaster layer of the fresco and any discontinuities that may be present. Thermography is essential to understand the integrity of the supporting wall of a fresco and make an accurate assessment of its structural health. A thermal image can also help to identify giornate di lavoro (regions of a days work), plaster detachments, delaminations, and the nature of cracks (as stable or otherwise risky). Figure 4.11 is a thermogram of the entire East wall of the Hall of the 500, Palazzo Vecchio, Florence Italy. Here the original windows can be seen filled in with bricks along the bottom portion of the wall. Figure 4.12 is a mosaicked composite of the right fresco panel from images taken in 2008. A large crack in both the fresco surface and the supporting wall appears darkened on the lower right side of the panel. This crack is, however, stabilized by the existing arch from an old doorway (filled in with bricks) below the stone frame. Faint gray squares, almost at the midline vertically, represent buca pontaia, the original holes that once held the artist's scaffolding.

Results of Technical Photography on the Fresco Mural

Figure 4.11. Thermogram of the East Wall of the Hall of the 500

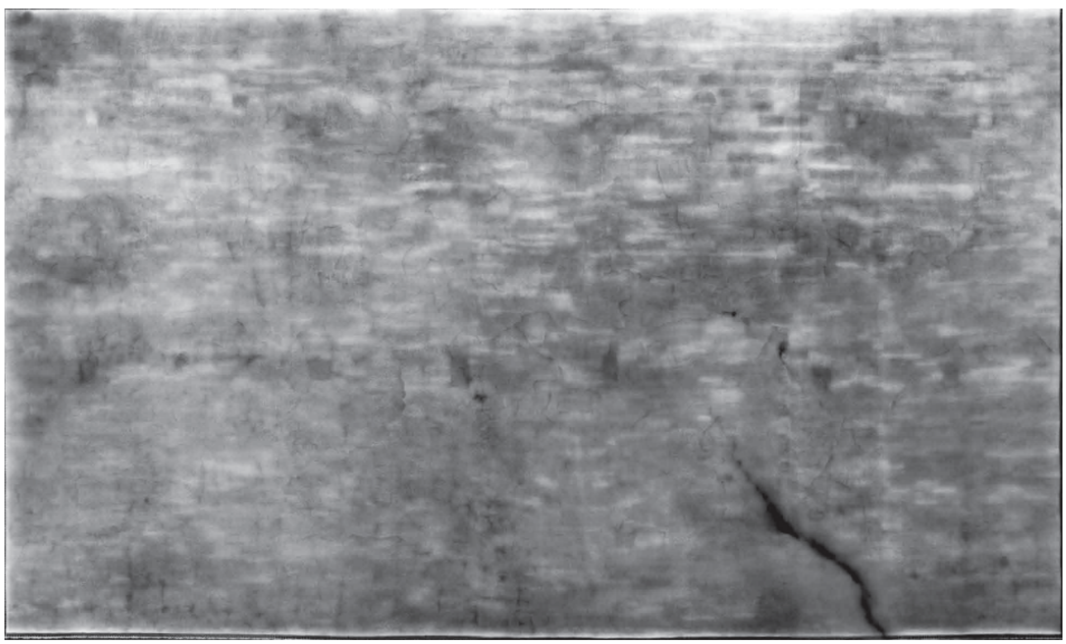

Figure 4.12. Detail thermogram of the fresco area, right panel.

Raking Light Imaging Taking images of the fresco in raking light (example above) provides information about the technique used by the artist. These images reveal incisions made in transferring the cartoon to the wet plaster surface and confirm that the fresco was completed with the true technique. Surface texture, deformities and cracks can also be documented with raking light.

Figure 4.13. Raking light detail of the fresco mural.

Figure 4.14. UV-induced visible fluorescence detail of the fresco mural.

UV Fluorescence Imaging The images to the right show a portion of the fresco taken under the illumination of ultraviolet light with wavelength approximately 380nm. A yellow filter is used to block the reflected light so that the visible fluorescence produced by the surface materials can be captured. UV fluorescence images are instrumental in identifying the materials present in the fresco. They especially can point out organic materials such as binding media, and the use of different pigments in repainted areas. The UV fluorescence image is surface sensitive, helps to document the effect of prior restoration efforts, and aids in determining where to do chemical point analysis. The image in figure 4.14 reveals evidence of repainted areas, spots caused by solvents, and the use of adhesive to reattach a piece of the fresco.

Infrared Reflectogram, 1.1um The infrared image can confirm features identified in the UV image, such as repaints. If a superficial spolvero is present it can also be seen in the IR.

Figure 4.15. Infrared detail of the fresco mural, 900-1100nm.

Figure 4.16. Infrared false color (pseudocolor) detail of the fresco mural.

Pseudocolor or False Color Infrared (IRFC) The detail images above show the superficial character of the white overpaint used during a 19th century restoration, which fluoresces blue in the UV image and appears pink in the pseudocolor IR. This image showing the infrared in false colors can help to identify repainted areas of the fresco.

X-ray Fluorescence (XRF) This non-destructive point analysis technique provides semi-quantitative elemental information about the materials that make up the fresco surface. It can help to identify the pigments used and confirm the presence of non–original materials. Due to the fact that data is only gathered at individual points (beam diameter approx. 4mm), it is best used after a full set of imaging diagnostics has been performed to pinpoint areas of interest. Here the use of natural pigments compatible with the buonfresco technique was confirmed, however in restored areas more modern pigments (like Zinc white) were found.

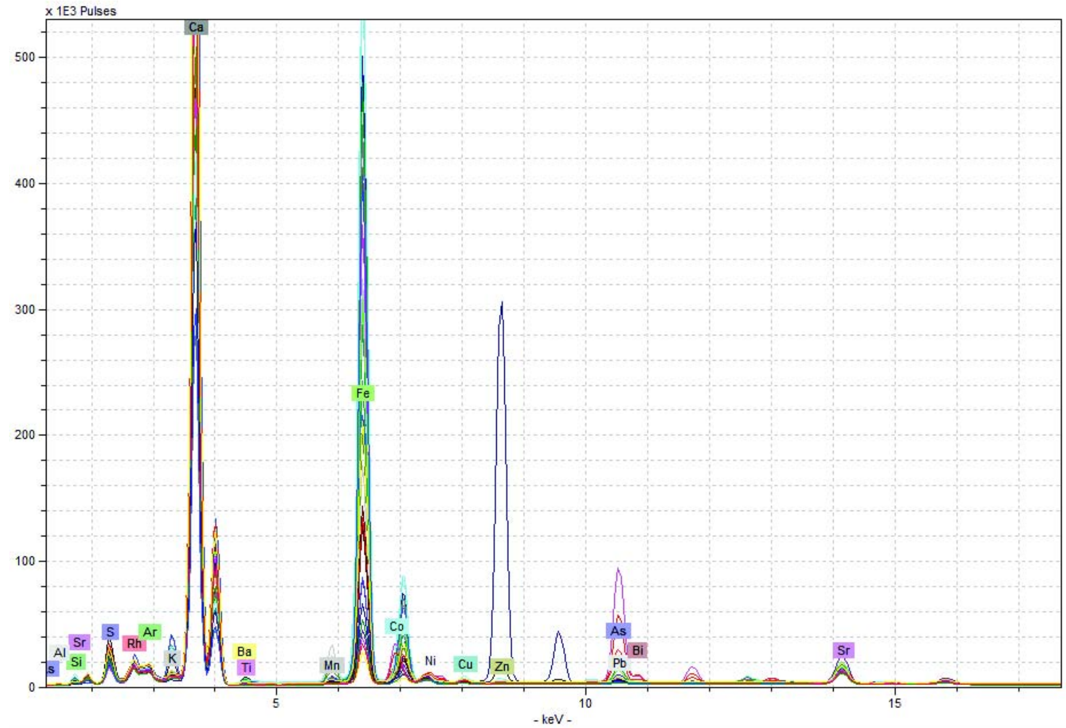

Figure 4.17. Spectra of all points analyzed plotted over the approximate 1 to 18keV energy range showing the spread of elements present in the pigments and plaster surface.

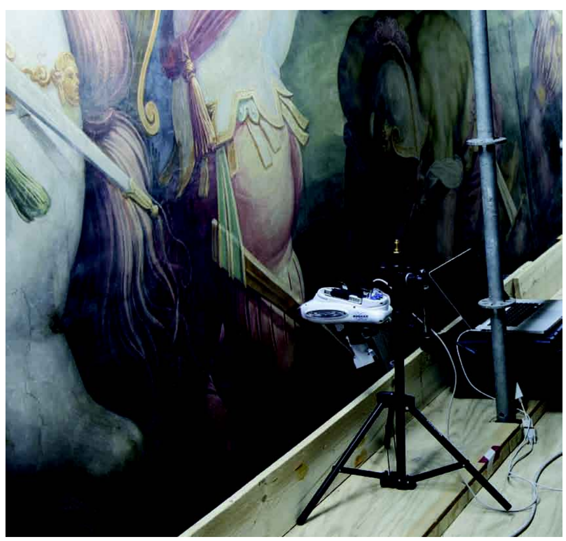

Figure 4.18. XRF point analysis using the Bruker Tracer III/SD mounted on a tripod.

Conclusions The comprehensive assessment for the state of conservation of a fresco relies on a multifaceted approach that takes into consideration the materials

Figure 4.19. Map of points analyzed, based on 2007 analytical campaign

Figure 4.20. Map of points analyzed, based on 2007 analytical campaign

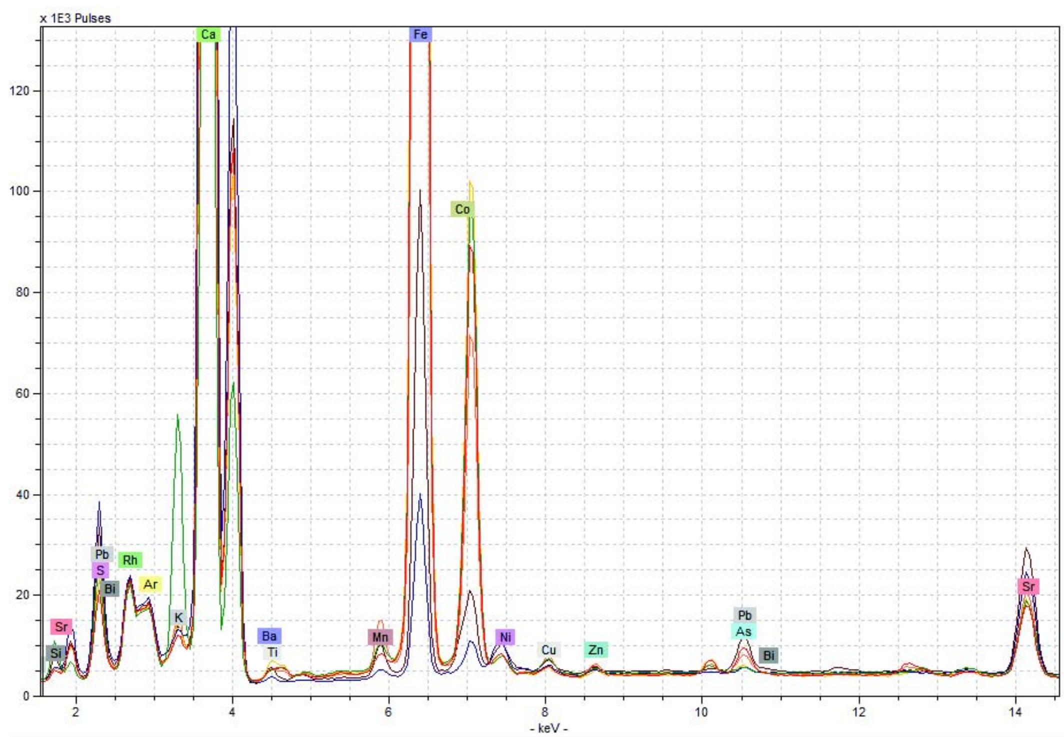

Figure 4.21. Spectra of selected points representing each of the colors present in the fresco palette. Point 9, green; Point 20, white; Point 7, yellow; Point 12, fleshtone; Point 33 gray/brown; Point 2, red.

present, the technique used, and the history of restorative efforts on the work of art. These objective data combine to create a scientific documentation that is useful to the stewards responsible for the conservation of this artifact.

4.2.1 Methodological Insights

In this section a fresco mural situated on a wall within a building was presented as the artifact of study. Fresco murals, as such, require portable instrumentation and fieldwork scenarios. They also require that a larger scale be accommodated with the infrastructure and technique.

Here the importance of a three-dimensional data scaffold is presented, over which multiple datasets may be aligned in the sense that information that was once just 2D, takes on a 3D significance. This concept can also be applied to objects, and tools are currently being designed to facilitate the full implementation of overlaid datasets, which afford the user new capabilities in visualization. This dissertation has been conceptualized with these advancements in mind.

The Vasari mural fresco documentation shows the difficulty of working in a grand space and over a large scale. This is a challenge best solved by robotic automation of the instrumentation, a preliminary design of which will be discussed in Section 5.1. It must be noted, that Section 5.2 also touches on the development of an augmented reality platform that would allow for an easier implementation of the methodological workflow in-situ in front of the mural.

The methodological insights gained from the fresco case study revolve around the concept of repeatability of exams or time monitoring of the condition of an artifact. It is the intention that this chemical imaging methodology be standardized and suitable for time monitoring. The case study allowed for a first exploration of what is actually involved if one intends to rigorously repeat a diagnostic exam. How congruous must the resulting datasets be? How identical must the setup be? The XRF points chosen for study were based upon a map of points analyzed in 2007 (from the Editech archives). Every reasonable attempt to return to the same point was made so that the spectra could be compared. This exercise through the fresco case study was fundamental to designing provisions for repeatability in the current method.

4.3 Wall Paintings: The Crucifix Chapel, Aci Sant'Antonio Sicily

The discovery of a series of frescoes is presented here for the first time, after they have been revealed in 2012 during a restoration carried out in the Crucifix chapel in the Mother Church in the town of Aci Sant'Antonio, Sicily. The mural paintings were preserved in each of the corners of the square chapel, behind an early 20th century counter wall. In this paper, we also show the application of multispectral imaging (MSI), portable XRF spectroscopy (pXRF) and Fiber Optics Reflectance Spectroscopy (FORS) for the identification of pigments on this interesting case of mural paintings. Documentation from the 20th century remodeling is available, and when taken into account along with this case study, represents an interesting case of “terminus ante quem” (TAQ) chronology since we are aware of the date when the last retouching to the square chapel walls could have been applied.

The Mother Church of Aci Sant'Antonio was originally built in 1566, and dedicated to Sant'Antonio. In 1693 it was rebuilt in the then current baroque style after a destructive earthquake occurred. The internal layout of the church forms a Latin cross with three naves, a transept and side chapels. Inside the church, several kinds of liturgical artworks are conserved, such as the wooden choir, and the frescoes by Pietro Paolo Vasta situated along the walls and the vault of the apse. Pietro Paolo Vasta (Acireale, 1697-1760) is considered one of the leading figures of Sicilian art. In 1734 the painter

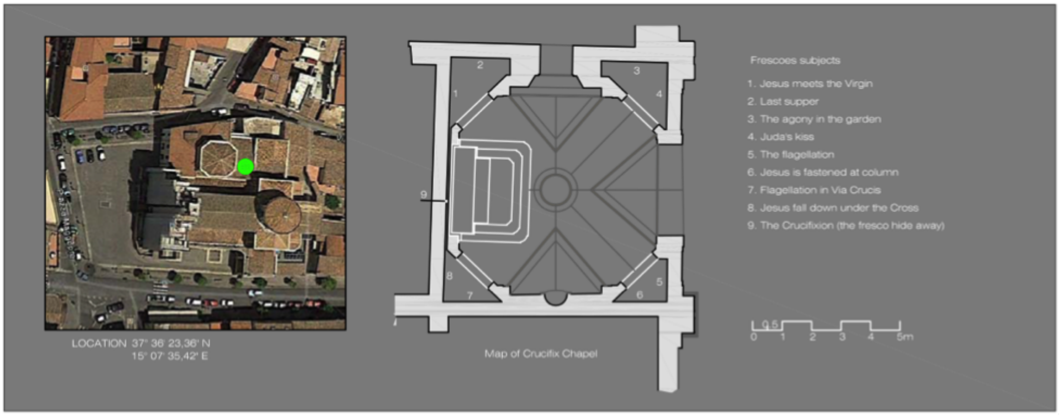

Figure 4.22. Crucifix chapel, Chiesa Matrice, Aci Sant'Antonio. Drawing of the floor plan with location of the frescoes and description of the scenes represented.

Figure 4.23. Crucifix chapel, Chiesa Matrice, Aci Sant'Antonio. Split panorama of the chapel after the renovation. The windows at each of the four corners allow the 17th century frescoes decorating the original chapel to be seen.

opened a workshop in Acireale where he received other artists as apprentices, such as Michele Vecchio, Alessandro Vasta (his son), and Giuseppe Grasso Naso. The Crucifix Chapel is the closest one to the apse, along the left nave, it has an octagonal floor plan (Fig. 4.22), which was realized within the original square-shaped one.

During the maintenance works on the ceiling, carried out between 2012 and 2013, the original shape and features of the chapel were revealed. The current octagonal arrangement is dated to the beginning of the 20th century, and the new walls are joined to the preexisting ones with tie-hooks in only a few places.

The discovery of the 18th century frescoes made it necessary to pause the current restoration work and reflect on the best way to represent the space. The choice was made to maintain the octagonal shape of the chapel, while making the frescoes in the corner niches visible by way of large windows (Fig. 4.23).

The original cycle of paintings was spread across the four walls of the square room. The paintings represent classic themes of the last days of earthly Christ: The Last Supper; The encounter between Christ and the Virgin Mary, which, in the Sicilian folk tradition represents the last moment before Christ ascends to Heaven (there are no traces of this episode in the Holy Scriptures); The kiss of Judas; and The Flagellation. The panel depicting the Crucifixion was absent from the central space above the altar of the chapel, where a 19th century altarpiece currently stands.

The mural paintings are made a fresco in wet plaster, with a secco (dry) finishing touches, as was common in the 18th century. This process allowed the artist better management of the retouching and working times. However, it also has the disadvantage of the end result being more delicate than the traditional buonfresco technique.

This cycle of frescoes is attributed to the painter Giuseppe Grasso Naso, pupil of Pietro Paolo Vasta, as the execution style corresponds to other mural paintings completed by the artist. Moreover, Don Vittorio Rocca, the priest of Aci SantAntonio, has found documentation, – the account book of the Mother Church for the period between 1768 and 1792, (Fig. 4.24) declaring a payment to Grasso Naso, and thus validating the attribution of the artwork to the Sicilian painter and dating the paintings to the 18th century. The painter would have worked in the chapel just a few years after Vasta had completed the frescoes in the presbytery. Overall, the paintings appear to be in good condition; however, those on the North wall (same side as the altarpiece) show signs of deterioration. Here, a substantial difference in the state of conservation occurs due to the presence of moisture,

Figure 4.24. Photograph of the archive showing financial transactions of the Parish from the month of August, 1773 to the painter Giuseppe Grasso Naso.

which has caused the plaster layer to crack, resulting in localized detachments. The construction of the octagonal chapel resulted in drops of lime ($CaCO_3 - nH_2O$) being splashed onto the adjacent paintings. Additionally, in several points it is possible to observe abrasions and holes from incidental damages caused by the equipment necessary to build the walls of the new chapel.

The frescoes are surrounded by a frame in trompe l'oeil, and the lower part of the frame is affected by a white film, which veils the painted layer. This may be caused by the higher level of moisture sustained by the lower part of the walls due to the capillary rise of water from the building foundation.

The presence of moisture must have been more evident before the 19th century and before the construction of later additions. The chapel was incorporated within the internal area of the church, making it protected from the weather to a height of about 3.8 meters. However, the wall where the altarpiece is positioned is external with respect to the church, making it more vulnerable in general to water damage. Therefore it remains that the upper part of the painted areas is drier and better preserved.

Access to the newly discovered frescoes is provided through the window openings in the walls of the octagonal chapel. To increase their readability and improve their appearance, a general restoration of the wall paintings will be carried out, involving the removal of all dust and surface dirt, consolidation of the deteriorated areas, and the reattachment of detached fragments of painted surface.

The main objectives of the scientific investigations presented in this paper, multispectral imaging, pXRF, and FORS were to identify pigments and localize areas of later retouchings on the wall paintings, thus obtaining very pertinent information prior to carrying out a cleaning intervention. To the best knowledge of the authors there is only one other published work on frescoes linked to the school of Paolo Vasta [45].

Instrumentation

Multispectral Imaging Used for the non-destructive identification of pigments [32, 4], this study illustrates MSI images in 3 spectral bands: Ultraviolet, UV (360-400 nm); Visible, VIS (400-780 nm) and Infrared, IR (780-1100 nm). The acronyms for the MSI methods presented in this paper highlight first the spectral band followed by R (Reflected), F (Fluorescence), FC (False Color). So the 5 imaging methods are called VIS (Visible), IR (Infrared), UVF (UV Fluorescence), UVR (UV Reflected) and

IRFC (Infrared False Color). It is mandatory to point out that, due to the nature of the painted surface, these optical methods are problematic and the user may be subjected to make interpretations and draw conclusions that remain uncertain. Therefore, to identify pigments with an acceptable degree of certainty, at least one other material specific technique must be employed, such as pXRF used in this study.

The MSI images presented in this paper were acquired with a Nikon D800 DSLR (36 MP, CMOS sensor) digital camera modified for "full spectrum", ultraviolet-visibleinfrared photography (between about 360 and 1100 nm). The CMOS sensor responds both to the near infrared and near ultraviolet ranges of the spectrum and the manufacturer installs an IR cut-off filter in front of the sensor to reduce infrared

Figure 4.25. The panoramic multispectral imaging system used to document the mural paintings in the Crucifix Chapel.

transmission. There are companies that remove this filter in commercial cameras, which are then said to be "full spectrum" [34]. The Nikon D800 camera was tethered to a computer to allow sharp focusing in nonvisible modes (IR and UV) using live-view mode.

The filters used for the MSI were: a) For Ultraviolet Reflected (UVR) photography, the B+W 403 filter together with the X-NiteCC1. The B+W 403 allows just the UV and IR light to pass, and the X-NiteCC1 is necessary to stop the IR produced from the UV lamp; b) For Visible (VIS) photography, just the X-NiteCC1 filter is sufficient; c) For UV Fluorescence (UVF) photography, the B+W 420 must be mounted to stop the reflected UV, and the X-NiteCC1 is also necessary to exclude any infrared from the UV lamp; d) For Infrared (IR) just the Heliopan RG1000 is used. A Nikon Nikkor 200 mm f/4 AI manual focus lens was used for all the MSI photos produced using the panoramic method [32]. Two 1000 W halogen lamps were used for VIS and IR photography; for UV photography, one high-Flux 365nm LED lamp was sufficient.

X-ray Fluorescence Spectroscopy The multispectral imaging was complemented by a qualitative elemental analysis carried out using portable x-ray fluorescence spectroscopy (pXRF), (Fig. 4.26).

Measurements were taken at an assortment of points selected to include each of the colors used in the palette in one or two different areas on each of the paintings. The instrument was operated in the field using a rechargeable Li-ion battery and a laptop computer for control and data storage. A total of 28 spots were analyzed, 13 on the painting the Kiss of Judas, and 15 on the painting the Flagellation. Spectra were subsequently processed and visualized using Bruker ARTAX software. The approach taken with the pXRF analysis was to acquire qualitative elemental readings on the materials present in the pigments used in the wall paintings. This was to be a quick

Figure 4.26. Acquisition of pXRF spectra on the Flagellation mural painting in the Crucifix Chapel.

point-based assessment that would serve to complement the more global analysis carried out with multispectral imaging.

Fiber Optic Reflectance Spectroscopy (FORS) A portable and miniaturized FORS system was used for this study [46]. Spectra have been acquired with the following parameters: integration time: 5 sec (integrating sphere); 5 msec (reflection probe); scans to average: 4; boxcar width: 5. The Ocean Optics integrating sphere ISP-R was used to take spectra on the same areas as pXRF analysis. The FORS spectra were compared with a database of pigments laid with the fresco technique [47]. Unfortunately, the FORS spectra of some of the pigments identified by pXRF (emerald green and chrome yellow) are not available and therefore a comparative evaluation could not be made.

Figure 4.27. Areas analyzed by pXRF and FORS on The Kiss of Judas mural painting.

The Kiss of Judas mural painting Green pigments. In areas 1 and 2, the paint has been applied a secco as evidenced by the numerous losses. The XRF spectra indicate Cu and As as the two major elemental components of the pigment. There are two arsenic-based green pigments: Scheele's green and Emerald green [47]. The first is ruled out because its color ranges from pale yellow-green to deep green and it is known to darken over time. Scheele's green, a copper arsenite of varying composition, was the first synthetic green copper arsenic pigment. Pigments known as Scheele's green comprise a group of copper arsenite compounds having widely variable compositions depending on manufacturing methods and the shade desired. It was introduced in 1778, and its use as an artist's pigment is scarcely documented. Emerald green, a copper acetoarsenite, is likely to be the pigment used in this painting. It was introduced between 1800 and 1814, and it is no longer available as an artists' pigment because of its toxicity; it has a brilliant blue-green hue, which matches the one observed in this mural painting.

The darker shade of green analyzed in area 6, is green earth as suggested by the

Scene	Area #	Color	Major Elements	Minor Elements	Pigments
Kiss of Judas	1	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	2	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	3	yellow	Cr, Fe, Pb, S	Ca, Sr, K	chrome yellow
	4	brown	Fe, Pb, Ca, S	Si, K, Sr	earth based
	5	white	Ca, S, Pb	Fe, Sr	calcite / gypsum / lead white
	6	dark green	Fe, Pb, Ca, S	Mn, Si, K, Sr	green earth / umber
	7	green	Pb,	Ca, Fe, S, Sr, Si	green earth / lead white
	8	white	Ca, S, Sr	Pb, Fe,	gypsum
	9	light green	Pb, Ca,	Mn, Fe, Si, K, Sr	green earth / umber
	10	red	Hg, Pb, S	Fe, Ca, Sr	vermilion / lead white / ochre
	11	red	Fe, Ca,	Hg, Pb, S, Sr	red ochre / vermilion
	12	blue	Pb,	S, Ca, Fe,	lead white / ?
	13	blue	Pb,	As, S, Ca, Fe,	lead white / ?
Painting	Area #	Color	Major Elements	Minor Elements	Pigments
The lagellation	1	red	Fe	Ca, Hg, Pb, S	red ochre / vermilion
	2	red	Fe	Ca, Hg, Pb, S	red ochre / vermilion
	3	tan	Pb		lead white
	4	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	5	tan/white	Pb		lead white
	6	brown	Pb,	Ca, Fe	lead white with earth
	7	brown	Pb,	Ca, Fe	lead white with earth
	8	white	Ca, S, Pb	Sr	calcite / gypsum / lead white
	9	tan/white	Pb		lead white
	10	tan/white	Pb		lead white
	11	tan/white	Pb		lead white
	13	green	Fe	Ca, Pb, K	green earth / lead white
	14	light blue	Cu, As, Ca, S	K, Fe, Sr	emerald green
	15	green	Pb, Fe, Ca,	Cr, Sr	green earth / veridian
	16	green	Fe, Ca, Pb	Cr, Sr, K	green earth / veridian

Figure 4.28. Summary of pXRF data for the two mural paintings analyzed, from [6]

iron content. The corresponding FORS spectra are flat and do not have characterizing features. The brighter greens, represented in areas 7 and 9, contain a considerable proportion of lead, and therefore they should be a mix of green earth and lead white, added to obtain the lighter hue. Lead white is a problematic pigment for frescoes since it is known to darken [48], however this problem occurs mostly on outdoor murals.

Results and Discussion

The Kiss of Judas and the Flagellation scenes on the East and West side of the South wall were examined. Figure 4.28 shows the list of areas examined with pXRF. The same areas were analyzed with the FORS system. The presence of some paint losses on the figures in both of the mural paintings allowed for the direct measurement of the preparation layer. Generally, the FORS analysis provided the same conclusions as the XRF analysis, (Fig. 4.28). For example, area 8 in the Kiss of Judas, was shown to be rich in calcium and sulfur. The calcium content is expected and compatible with the fresco technique; however the elevated presence of sulfur is likely due to on-going degradation processes, both organic and inorganic, which lead to the formation of sulfates in the superficial patina [49].

Yellow pigments. On the bottom border of the mural, area 3 is shown to have been retouched with 19th century chrome yellow [50]. This is a relatively inexpensive yellow pigment with high covering power, which was in use (along with the other chrome pigments) by 1816 but on a limited basis. Because the pigment tends to oxidize and darken on exposure to air over time, and it contains lead, a toxic, heavy metal, it has been largely replaced by cadmium yellow in today's market. This chrome yellow paint appears to have been applied over an older and original yellow layer of paint, which analyzed in area 4, confirmed a more typical yellow earth (yellow ochre or umber). The FORS spectrum shows the characteristic S- shape and the presence of two broad absorption bands near 660 nm and 930 nm, which are attributed to goethite, confirming the identification of yellow ochre (Fig. 4.29).

White pigments. A thin layer of lead white, analyzed in area 5, has been used to whitewash the original caption. However, most of it has disappeared and the original caption is almost entirely readable.

Red pigments. As shown by the IR image, a red pigment used for Jesus' vest

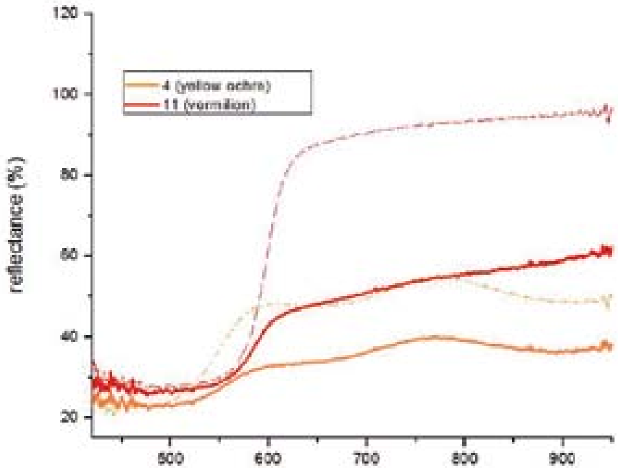

Figure 4.29. FORS spectra of areas 4 and 11 on the Kiss of Judas mural painting. Dotted lines are the reference spectra of corresponding pigments applied on fresco. from [7].

strongly reflects IR, which rules out the use of red earth pigment. Complementary to this information, the pXRF spectrum shows that the pigment is rich in mercury, (areas 10 and 11) confirming the use of vermilion. This identification is supported also by the FORS spectrum of area 11, (Fig. 4.29).

Blue pigments. The blue pigment for Jesus' mantle absorbs the infrared and turns a reddish/purple color in the IRFC, (Fig. 4.31). Two areas (12 and 13) were selected on the mantle for pXRF analysis and lead was the only element shown to have a significant contribution to the spectra. The FORS spectra are flat and do not help in the identification. The lead content observed in the pXRF spectrum likely belongs to lead white used to brighten the blue pigment. Since the spectrum presents no other major peaks, it stands to reason that the blue pigments based on metal elements (azurite (Cu), Prussian blue (Fe), Cobalt blue (Co)) are not present in the areas studied. In this case, we may rule out some blue pigments, however, a blue pigment identification cannot be positively confirmed using only the techniques employed in this preliminary study.

Figure 4.30. Areas analyzed by pXRF on the Flagellation mural painting.

The Flagellation mural painting Red pigments. The pXRF spectra of areas 1 and 2 show a large content of mercury, which together with the high infrared reflectance observed in the FORS spectrum, confirm the pigment vermilion.

White pigments. Lead white was used for the pavement, confirmed in the analysis of areas 3, 5, 6, and 7. Lead white was also mixed with ochre on the drape, evidenced in the spectra from areas 9, 10, and 11, which show an elemental content composed mainly of Fe and Pb.

Green pigments. The same arsenic-based Emerald green is found in the bluish-

Figure 4.31. The Flagellation mural painting. Visible (left) and details: visible (top left), infrared (top right), infrared false color (bottom left) and UV fluorescence (bottom right).

green band on the border, analyzed in areas 4 and 14. Green earth is found on the lower green decoration, area 13, and on the pedestal, areas 15 and 16, also with some viridian, as indicated by the chrome content. Pannetier, a color maker in Paris began to make chromium green in 1838 and viridian soon replaced the toxic Emerald Green.

Both murals proved to be completed with a similar palette of typical earth based fresco pigments. Vermilion was found on both of the two murals. This is a relatively expensive pigment for murals where red ochre would instead be more commonly used. An interesting note was that in all of the spectra, except those of the light blue areas, there was an abundance of lead, indicating the extensive use of lead white throughout the

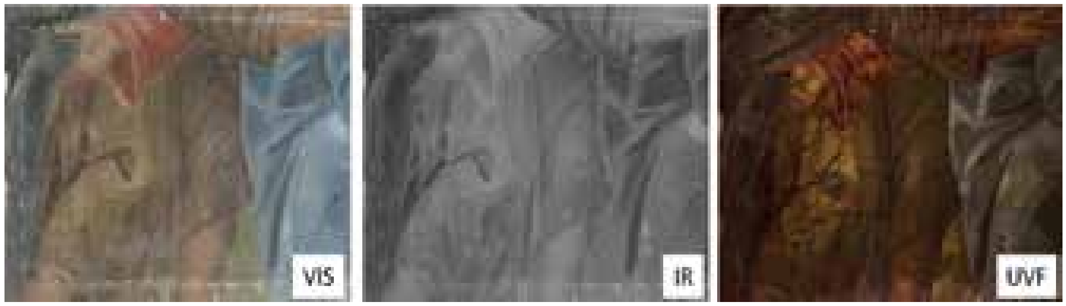

Figure 4.32. Flagellation, area where a cleaning test was performed, framed by the dotted white line. UV fluorescence is evident on the dress highlights.

paintings. The light green areas showed a high concentration of both copper and arsenic in the ratio of 1:1, in accordance with the composition of the pigment emerald green.

We can tell by the close observation of Jesus' right hand, that the underdrawing was probably performed by tracing the outline of the figures using a dark brown pigment and thin paintbrush (Fig. 4.32). The main scenes of the Passion are in a quite good state of conservation, but the decorative frames seem to have been refashioned several times over the centuries.

The ultraviolet radiation excites the organic molecules present on the surface of the artwork, producing a pale fluorescence and revealing the presence or the alteration of organic components present on the surface. In this way, it is possible to locate and assess the presence of a biological colonization (some bacteria have their own peculiar fluorescence), of retouches made by the artists themselves, of particular organic colorants, or previous restoration compounds.

Figure 4.33. The Flagellation. A secco retouches exhibit strong UV fluorescence.

In the fresco technique, the principal paint binder used to fix the pigments to the substrate is slaked lime. Once the fresco is dry, the artist is able to make final retouches and details using the tempera technique (egg yolk and/or milk). While calcite doesnt emit fluorescence under UV light, the paint bound by tempera does. In figures 4.32 and 4.33, tempera retouchings on the dresses, the details of the faces, the floor tiles, and the hands, are indicated by their UV fluorescence.

Conclusions

It was shown that the mural paintings have been carried out using the same palette, which has been documented in contemporary frescoes from the same school of artists operating in Sicily [45]. Viridian is the only modern pigment found on the figures. More extensive interventions with 19th century pigments (emerald green and chrome yellow) were found only on the bottom border of the mural paintings, which is clearly subject to more aggressive degradation caused by capillary rise of water from the building foundation. A number of restorations were likely performed before the damaged walls of the chapel were eventually enclosed during the 20th century remodeling, and the memory of the frescoes lost to the community until their recent rediscovery.

4.3.1 Methodological Insights

The scenario where historic wall paintings were uncovered behind the walls of a formerly square chapel made octagonal, posed an analytical situation with many open-ended questions to be answered. Identifying the palette was of utmost importance to the study for the historical clues it may provide. Additionally, since the area had most certainly undergone several phases and treatments over the centuries, it was important to understand the diversity of the materials present, both inorganic and organic. In this scenario, stakeholders responsible for ensuring the ability of the public to appreciate the architectural history and works of art from different eras, as well as, for the general maintenance and safety of the building were depending on the results of the interdisciplinary investigations.

In this case the artworks were termed “wall paintings” instead of fresco because the technique of execution did not rigorously subscribe to that of a true buonfresco, as was used by Vasari in the second case study. This was evidenced by the presence of organic materials and binding media used to extend the pigments. Additionally, the technique was more indicative of the trend during this later time period (18th century).

It was important to determine the pigments used because it is likely that these wall paintings, having just recently been discovered behind a current wall, will need to undergo some sort of cleaning, consolidation or treatment to preserve them for viewing. In addition, the date of execution was not precisely known in this case, or the history of any retouchings or alterations. The palette could potentially give indications to time period in this case, since many new pigments were only synthesized in the 18th and 19th centuries.

The wall paintings scenario represents a situation with many unknowns where paint has been potentially applied with several different binding media, and has aged in an unknown fashion due to unique environmental conditions as the architecture of the chapel evolved over the centuries. The chemical imaging methodology deployed in this field scenario, combining technical photography and point-based XRF spectroscopic analysis served to assess the state of conservation and identify the pigment materials used. In this case these preliminary examinations were subsequently complemented by other exams both non-invasive and sampling based [24].

4.4 Summary of Field Applications

The field case scenarios provided a variety of opportunities to work in different environments and with diverse collaborators. In each case, the objectives were similar; to deploy portable equipment in order to collect a suite of technical photography images, and to study the painted surface with point based XRF spectroscopy in attempt to define the palette of pigments used. These experiences were important to develop a methodological procedure. Each case study has been published and discussed by peers at meetings.

Chapter 4, in full, is a reprint of the material as it appears in S. Stout, F. Kuester, M. Seracini. "XRF Assisted, Multispectral Imaging of Historic Drawings" Advances in X-ray Analysis, 56, (2012); A. Cosentino, S. Stout, R. Di Mauro, C. Perondi. "The Crucifix Chapel of Aci Sant'Antonio Newly Discovered Frescoes" Archeomatica, 2, (2014); and the conference poster "A comprehensive methodology for the analysis of a 16th century fresco mural" presented August, 2012 at the 1st Gordon Research Conference in Scientific Methods for Cultural Heritage Research, Mt. Snow, Vermont. The dissertation author was a primary investigator and author of these papers.

Chapter 5

Advanced Applications: Creating New Tools for Exam Implementation

5.1 The WAVEcam Robotic Hybrid Platform

The WAVEcam has been designed to automate and accelerate the workflow for technical photography and spectroscopy in the digital documentation of relatively planar cultural heritage artifacts. The imaging platform allows for customized usage scenarios through the ability to design and fabricate mounting brackets based on need. In this case-study based demonstration of the WAVEcam, we show enhancements of the typical workflow, including speed, resolution, and user involvement through the implementation of technical photography (acquiring multispectral mosaic images), and x-ray fluorescence point-based spectroscopy for heritage documentation and diagnostics. The WAVEcam is a robust ultra-high resolution imaging platform uniquely adapted to acquiring images for wide-angle visualization environments.

Introduction

The documentation of cultural artifacts serves as a record of their state-of-conservation, as well as, a method by which they can be preserved through digital archives [51]. Imaging, collecting a visual representation of the work of art, is perhaps the most fundamental procedure for preservation and has been previously reviewed [52]. At present, imaging spectroscopy is becoming the state-of-the-art through systems that are primarily laboratory based [27]. In the early 1990's the VASARI project constructed one of the first portable imaging scanners to document paintings [53].

Technical Photography (TP) makes up the basic set of diagnostic images which are acquired. Over the years, several research groups have designed custom X-Y scanners for the purpose of mosaic imaging and spectroscopy [54, 55, 56], and recently, the panoramic technique has also gained popularity due to the wide availability of tools such as the Gigapan [36]. Robotics have been applied to imaging, mostly in other scenarios requiring remote surveillance [57, 58, 59]. In an effort to design a system that would be easily assembled, modular, and based upon off-the-shelf parts, as well as include a third mobile axis offering more precision control and versatility, a commercial 3D printer has been adapted for use as the basic infrastructure for the scanner. This solution to precision scanning is designed to be more accessible to a wide variety of users.

The ultra-high resolution imaging platform is currently being developed to operate in tandem with a wide-angle visualization environment (WAVE), a highly versatile multi-screen display system. The WAVEcam robotic imaging platform has been designed for the technical photography of cultural artifacts which may be accommodated on a horizontal table-top with a one square meter surface area (e.g. paintings, drawings, manuscripts). The instrument is equipped with precision rails and a mounting head, which operate above the object in the x, y, and z directions, and the movement may be programmed using g-code. The WAVEcam facilitates the acquisition of high-resolution mosaicked images, taken in a series of multiple shots for focus stacking, and is designed to operate autonomously after the appropriate settings are input by the user. Especially relevant in the practice of technical photography of paintings, where high-resolution images are acquired in different wavebands, the WAVEcam affords the capability to precisely

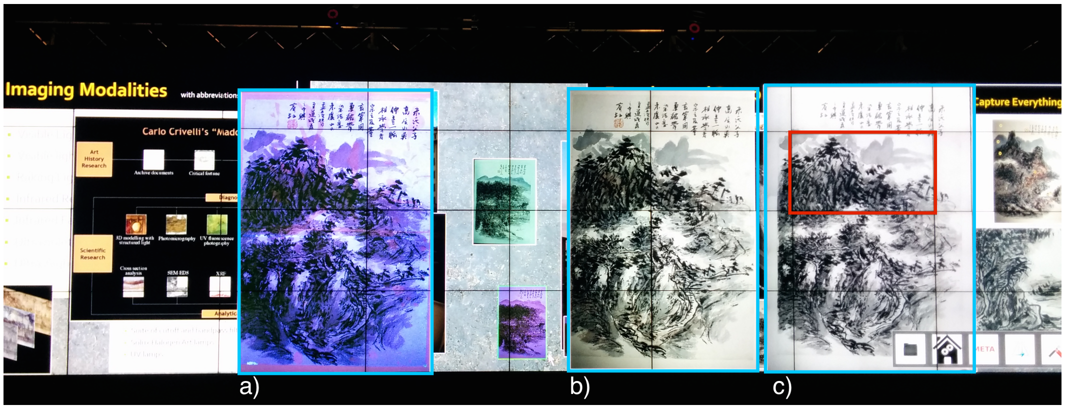

Figure 5.1. Technical images indicated by blue boxes in the a) UV Fluorescence, b) Visible, and c) Infrared wavebands displayed on a WAVE large format display. Individual screen size, indicated by red box, measures 48” diagonally (resolution: 1920x1080 pixels).

overlap single shots from subsequent imaging runs. The autonomous robotic nature of the instrument has drastically reduced the user time commitment for the acquisition of technical photography images of paintings, while improving the performance in terms of resolution able to be realistically achieved.

The implementation of the WAVEcam described here is illustrated through the documentation of watercolor landscapes by the Chinese artist Huang Binhong (1865-1955). Over the span of two working days the imager captured a full diagnostic set of images (ultraviolet fluorescence, near-infrared, and visible wavebands) for 5 paintings measuring approximately 36cm by 42cm. An example of the images displayed on the WAVE, (Fig. 5.1).

For one painting in particular, we increased the resolution by decreasing the size of each tile, effectively acquiring 1820 shots in 364 locations in both the visible and infrared wavebands. Additionally, a spectroscopic survey of several points was carried out using a non-invasive portable XRF (Bruker III-SD; Kennewick, WA) mounted to the robotic head via a custom printed mount.

5.1.1 Architectural Design

Imaging Approach By using a camera mounted to a 3D printer, programmatic control is gained over the camera position, camera triggering, and timing. Camera motion is programmed with the 3D printer's native g-code protocol, which provides control of the camera position in x, y, and z, as well as delaying between movement commands. Camera triggering is accomplished by attaching an optoisolator to one of the 3D printers fan outputs, allowing programmatic control over when the camera takes an image. A MATLAB program to generate the appropriate g-code to image an area of the print bed was written to accept the coordinates of the corners of the area of interest, as well as the desired height to ensure focus, and then generate the appropriate g-code. Several parameters are considered to generate the g-code positions for imaging.

In order to ensure sufficient overlap for stitching, the camera field of view is overlapped with the next camera position by 50 percent. Beyond ensuring that there are sufficient features for stitching, 50 percent overlap enables the stitching algorithms to select sharper detail from the center of the image frame, as opposed to the edges or corners, where corner softness and lens aberrations are more apparent.

When using macro lenses, the depth of field is particularly shallow, making it difficult to image an artifact with a 3D profile, or even a painting which does not lay perfectly flat on the print bed. To counteract this, we use the technique of focus stacking – taking multiple images from slightly different distances to capture images with good focus for the parts of the artifact which are at different heights. In post processing, the sharp portions of each image can be isolated and combined to provide an image which is sharp across the whole frame, regardless of distance. To accommodate this, 3 or 5 images are shot at different z heights for every (x,y) position.

Surface Interpolation In most cases, the assumption that the painting being imaged is flat does not hold. This is especially true for canvas paintings stretched over a possibly warped wooden frame and positioned laying horizontally [53]. To solve this, the software control of WAVEcam's vertical axis is programmed to match the path of the camera closely to the curvature of the painting surface. The variability across the painting surface is first assessed by traversing along the edges, and in the center of the painting, moving the motion stage up and down, and recording the height that gives the best focused image at each point. From there it can be determined whether or not it is necessary to utilize the surface interpolation feature built into the path planning software.

If the painting is determined to be sufficiently planar and parallel to the WAVEcam's bed for the current lens, then the camera will be moved in a flat plane for the sake of simplicity. However, in the event of a warped or uneven surface a biquadratic interpolation between 9 sample points at the corners, edge midpoints, and centroid is used. A bilinear interpolation between the 4 corners was initially considered, which would help compensate for planar but slanted surfaces such as paintings bound in books that do not sit flush on the imaging bed. However, it was also necessary to compensate for the smooth curvature formed by the sag usually present in the center of canvas paintings stretched over wooden frames. Biquadratic interpolation permits a close match the smooth curves of a warped painting with minimal time spent gathering z-height information.

The paintings by Huang Binhong presented in this case study are bound in a book which lies sufficiently flat on the imaging bed when held down with felt-padded metal weights on the corners and edges. In other test-cases, over 3mm of sag was observed in the middle of an oil painting on canvas, which necessitates the use of 9-point biquadratic interpolation for movement of the camera to acquire macro photography over the surface. Figure 5.2 is an example of an exaggerated displacement map shown here to visually represent the sort of curvature compensation possible with biquadratic interpolation.

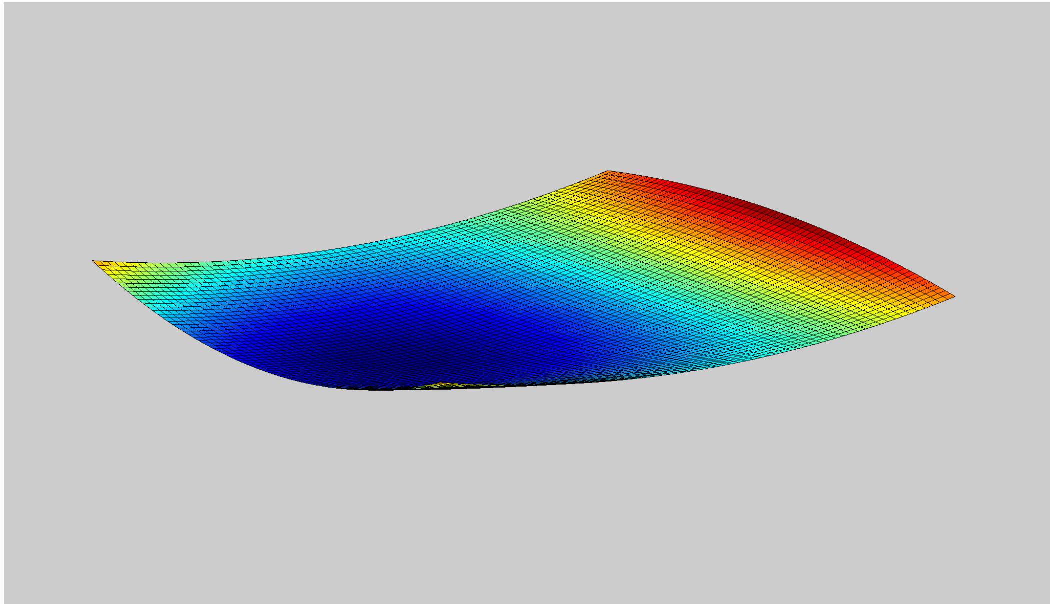

Figure 5.2. Exaggerated curvature of warped painting interpolated over 9 measured points.

Motion Stage Construction For our motion stage a professional quality 3D printer from 3DP Unlimited was adapted as the infrastructure for the scanner. Two-axis precision precision motion stages are not uncommon for taking mosaic images, the real advantages of the system are threefold. Firstly, the addition of an even higher resolution third motion axis allow us to adjust the system for different sensors and lenses at the push of a button, as well as adjust the imaging distance minutely during the imaging process to adjust focus for lens distortion and surface unevenness automatically. Secondly, its other purpose as a 3D printer allows easy adaptation for new sensors and equipment in the field. Finally, the motion stage comes pre-assembled and tested from the manufacturer as a professional quality instrument with extremely high quality parts.

This motion stage is constructed from large linear rails designed by PBC Linear to perform CNC milling and routing for years without maintenance. While this may seem overkill for the task of moving a camera around, we gain significant advantage from its construction. Firstly, the real world use of such a device inherently requires it to be transported and accidentally abused. When imaging paintings two orders of magnitude more valuable than the imager itself, failure is not an option. Secondly, we take full advantage of the 0.008mm resolution in the XY direction and 0.0025mm resolution in the Z axis. While this XY resolution may not be necessary for creating a single mosaic as stitching software is used to align pictures, precisely overlaying one mosaicked image on top of another is required to compare the diagnostic images in different wavebands. Therefore, repeatability and precision must be on the order of a single pixel size, which is the case here with even the highest resolution tested. To eliminate the effects of hysteresis, multiple image runs in different wavebands are carried out by following the exact same motion path (also without moving the painting). More useful than the XY resolution, is the 0.0025mm resolution of the Z axis to allow precise control over the camera's distance to the painting. Macro photography is particularly sensitive to the position of camera relative to the subject due to the small depth of field. We take full advantage of this resolution to position the camera such that different sections of the frame are in focus in consecutive photographs. These consecutive images are later focus stacked to produce a final mosaic that is consistently in focus.

Field Curvature Compensation The design goals of this unit and its control interface were aimed at working with standard off-the-shelf cameras and lenses to both reduce cost and give the user the widest selection of imaging capabilities. Since most photographic lenses are not field flattening lenses and most cameras use flat sensors, the Petzval field curvature must be compensated for by taking multiple images of each section of the painting at slightly different distances such that each area of an item is in focus in at least one of the images taken. These images are then merged together with the process of focus stacking such that only the focused areas are used for the final mosaic [60].

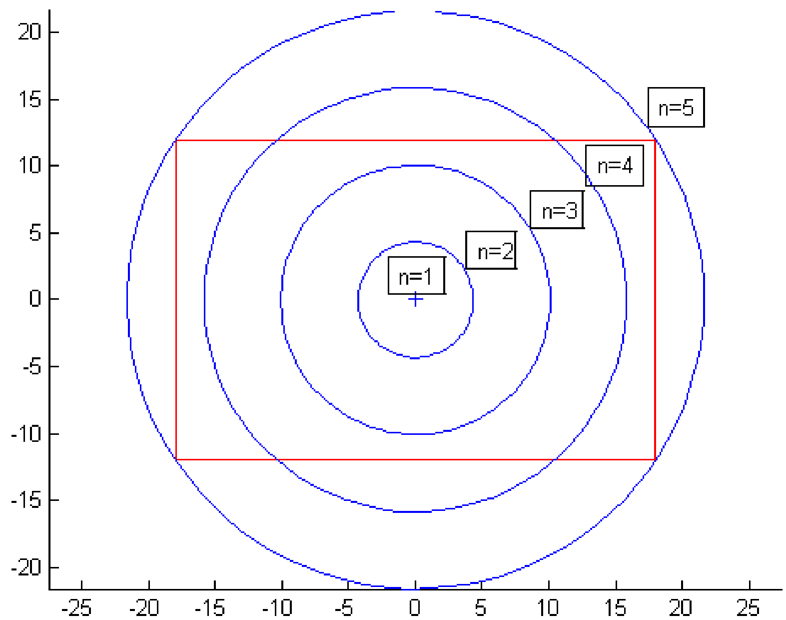

Figure 5.3. Maximum resolution imaging approach, based on five focused rings evenly spread over a 36mm x 24mm frame.

For an uncorrected lens and flat sensor, the surface in focus is a sphere centered around the focal point of the lens. Thus, we segment the camera's field of view into concentric rings where this sphere intersects the painting at a varying set of n distances from camera to painting, (Fig. 5.3). While it would be possible to take n pictures at even intervals between the distance h_m which puts the middle of the frame in focus, and h_c that puts the corners in focus, this would result in uneven radial distances between rings in focus.

Instead, the camera heights h_n necessary to ensure each region of the painting is within a given distance from a focal ring are calculated to arrive at as few images taken as necessary. To do this, the radius of the Petzal field curvature of the lens being used must be known. This curvature may not necessarily be centered around the focal point of the lens as lens manufacturers sometimes attempt to flatten this curvature to reduce this very problem. Thus, it can be determined experimentally once per lens. This also saves the trouble of measuring the location of the lens relative to the Cartesian coordinate system of the motion stage.

The process is as follows, the motion stage is moved up and down above the painting to collect two data points. The first data point is the motion stage height h_m that puts the middle of the frame in focus. The second data point is the motion stage height h_c that puts the corners in focus. The difference between these is d_h No manual measuring of the camera or lens mounting is necessary, nor is any prior knowledge of the lens focal properties needed.

$$d_h = h_m - h_e \tag{5.1}$$

From the framing experiment, the distance from the center of the image to the corner is now known. This is then termed the frame radius.

$$\begin{aligned} r_f &= \sqrt{(w_f/2)^2 + (h_f/2)^2} \\ \text{where } r_f &= \text{frame radius} \\ w_f &= \text{frame width} \\ h_f &= \text{frame height} \end{aligned} \tag{5.2}$$

Seeking to find the radius of the field curvature, called r_c, the small angle θ is defined from the center line of the camera's lens axis to the corner of the frame that was put in focus. Both θ and r_c are unknowns so two equations are given by the geometry of the triangle formed by the center of field curvature, the center of the frame, and the corner of the frame.

$$\sin\theta = \frac{r_f}{r_c} \tag{5.3}$$

$$\cos\theta = \frac{r_c - d_h}{r_c} \tag{5.4}$$

The Pythagorean identity is then applied to eliminate the variable θ and combine the two equations.

$$[\frac{r_f}{r_c}]^2 + [\frac{r_c - d_h}{r_c}]^2 = 1 \tag{5.5}$$

Rearranging solves for the radius of curvature.

$$\begin{aligned} r_f^2 + r_c^2 - 2r_c d_h + d_h^2 &= r_c^2 \\ r_f^2 + d_h^2 &= 2r_c d_h \\ r_c &= \frac{r_f^2 + d_h^2}{2d_h} \end{aligned} \tag{5.6}$$

The camera is then positioned at n heights such that the $n+1$ rings are in focus. The tallest height h_1 will be the position measured to have the very center of the image in focus. In figure 5,this ring becomes a simple point in the middle. The lowest height h_n will have only the extreme corner exactly in focus. Let the radial distance between rings d_r be given as

$$d_r = \frac{r_f}{n-1} \text{ for } n > 1 \tag{5.7}$$

The choice of the number n images taken at each camera position is entirely based on the user's subjective evaluation of the example images taken during the experiment and ranges with different lenses and zooms. Between 3 and 5 images per location are taken depending on time constraints.

$$h_i = h_m + r_c - \sqrt{r_c^2 - [d_r(i-1)]^2} \quad \text{for } i \in [1, n] \tag{5.8}$$

Since the original height measurements h_m and h_c were taken in the coordinate system of the motion stage, the required motion stage vertical heights h_i are output based on equation 5.8.

5.1.2 Experimental Setup of Instrumentation

Technical Photography of Paintings

The WAVEcam has been designed to follow the method previously described [4], [61] for the technical photography of paintings. Additional references were also consulted [11], [62] to inform the workflow. The camera has been modified from its off the shelf state to have the internal infrared filter removed, thus making the CMOS sensor sensitive to 1100nm [34]. A selection of bandpass filters allowed for the various waveband imaging modalities to be captured [4]. An abridged selection of TP images was chosen based on the lighting scenarios and filters involved, to accommodate the time constraints we had while working with these rare artifacts.

Imaging Equipment The Nikon D810 DSLR camera was selected as the sensor to gather the multi band imagery with high spatial resolution. The D810 is a high-end DSLR featuring a 36 megapixel sensor, delivering the highest spatial resolution possible without requiring use of an expensive specialized sensor.

The Nikon AF Micro-Nikkor 200mm f/4D macro lens was selected to be able to

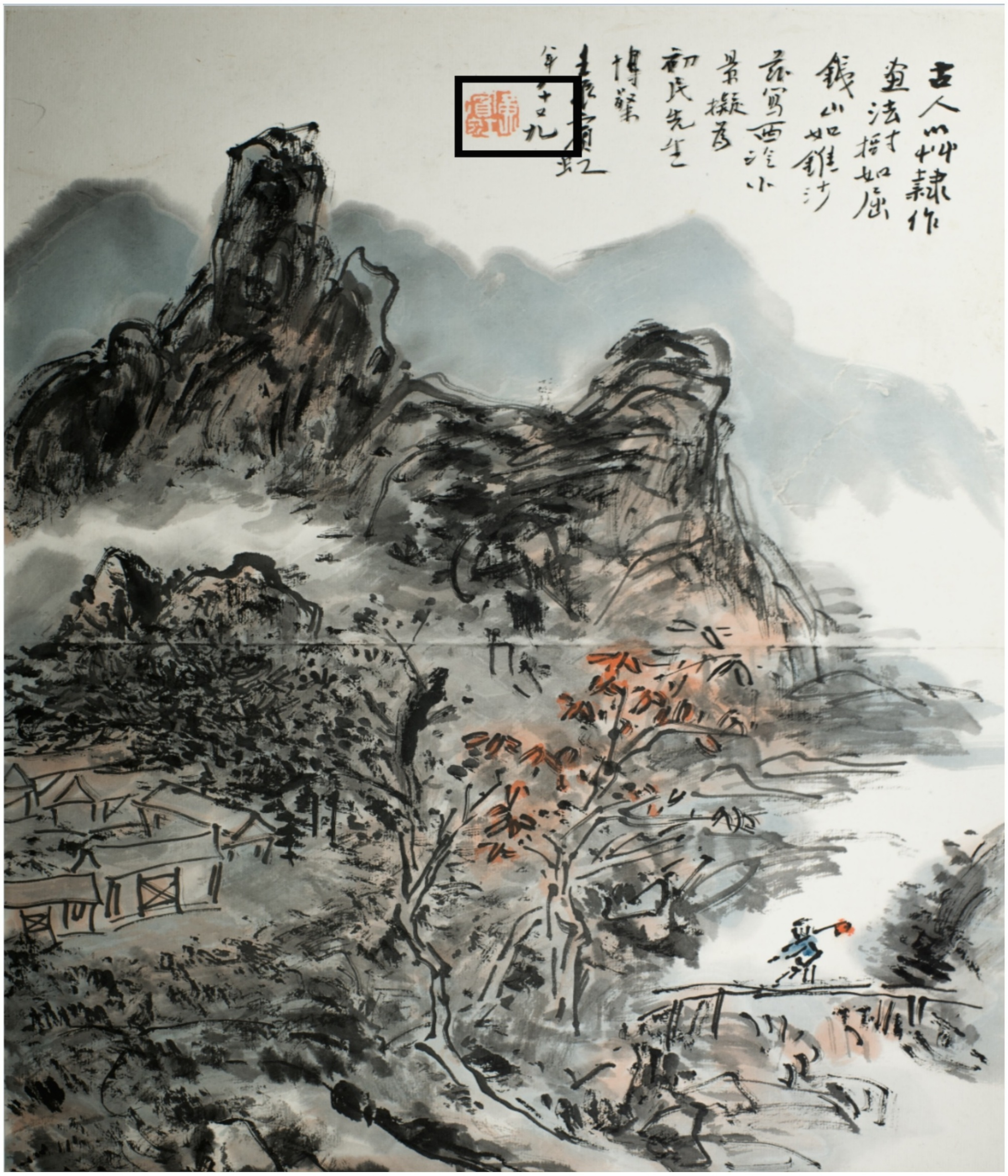

Figure 5.4. One watercolor from the collection showing the level of detail achieved through the WAVEcam imaging campaign. The final mosaic of 1820 images was 6 gigapixels and had a pixel size of about 6um.

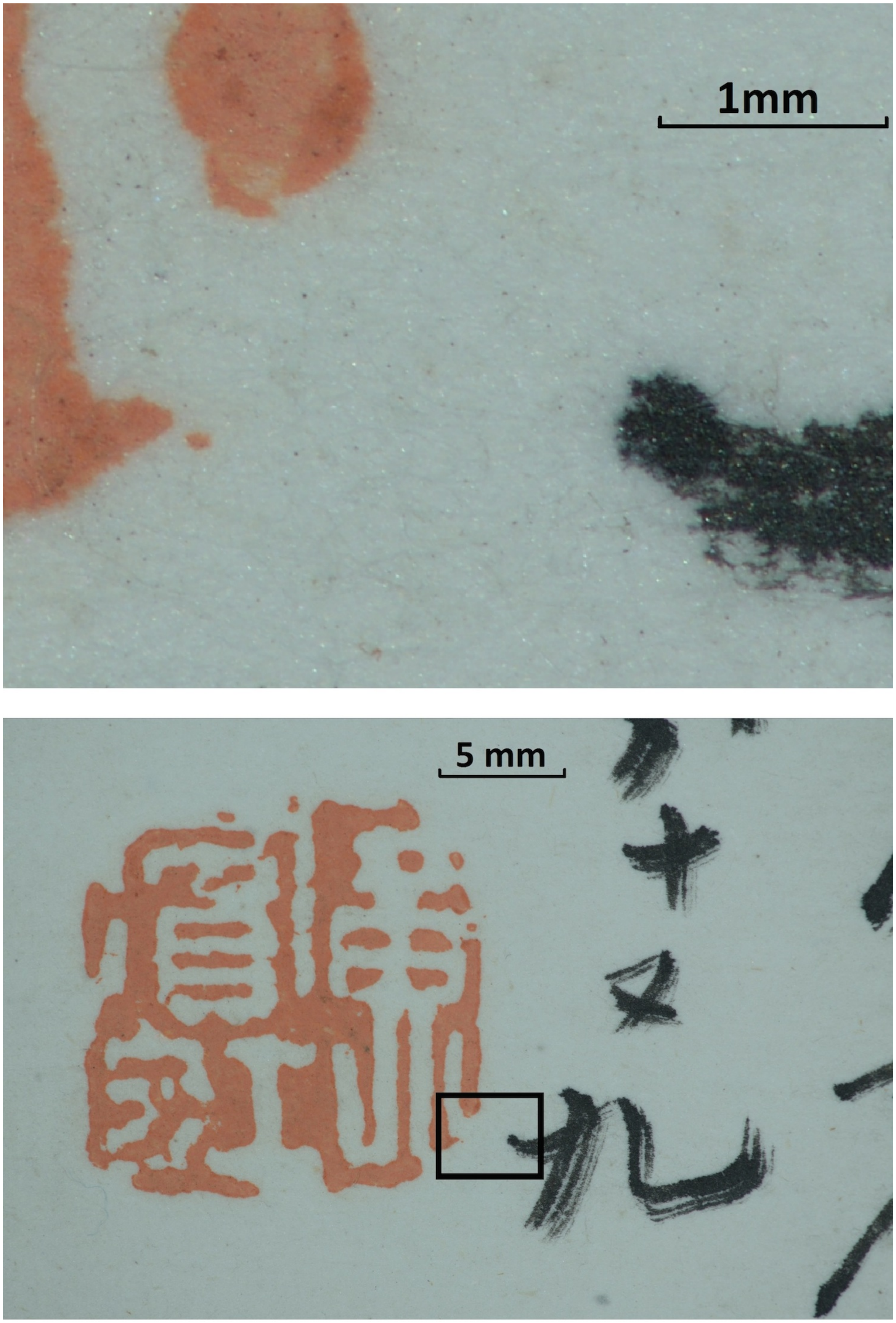

Figure 5.5. Detail focused on calligraphy and artist's stamp.

deliver a 1:1 reproduction ratio, which provides a resolution of 6 microns across a pixel, while still maintaining a safe working distance to the artifact, minimizing concerns of contact between the imager and the artifact.

To meet the time constraint of scanning multiple artifacts in a limited amount of time, the Nikon AF-S NIKKOR 24-120mm f/4G zoom lens was selected, which provides the flexibility of changing the focal length to accommodate different spatial resolution requirements. Imagery with a resolution of up to 20 microns across a pixel can be captured using this lens.

Lighting and Sensor Mounting The major infrastructure used in building the WAVEcam began life as a 3D printer, and careful thought has been applied to allow the simplest conversion possible back and forth between printer and imager. This is mostly because 3D printed components are made on the device itself. The motion stage provides two identical flat vertical mounting surfaces. For printing, both are used to hold dual plastic extruders to support multiple materials. Three new attachments have been designed and fabricated to re-use these surfaces. New mounts and fixtures can be made on the fly in the field with little other equipment necessary. However, a set of three mounts serve the full extent of this case study. First, a vertical bracket is necessary to support standard DSLR cameras. While the motion stage provides enough vertical range of motion for a wide range of lenses, we include a 30cm slot to allow positioning the camera in such as way to guarantee it cannot interfere with the painting through the full range of motion. A lighting fixture is also printed and mounted to the secondary mounting surface to move with the camera. This ensures consistent lighting regardless of the camera position. Both of these parts are seen in red in figure 5.6. Not shown is a similar mount for the XRF unit.

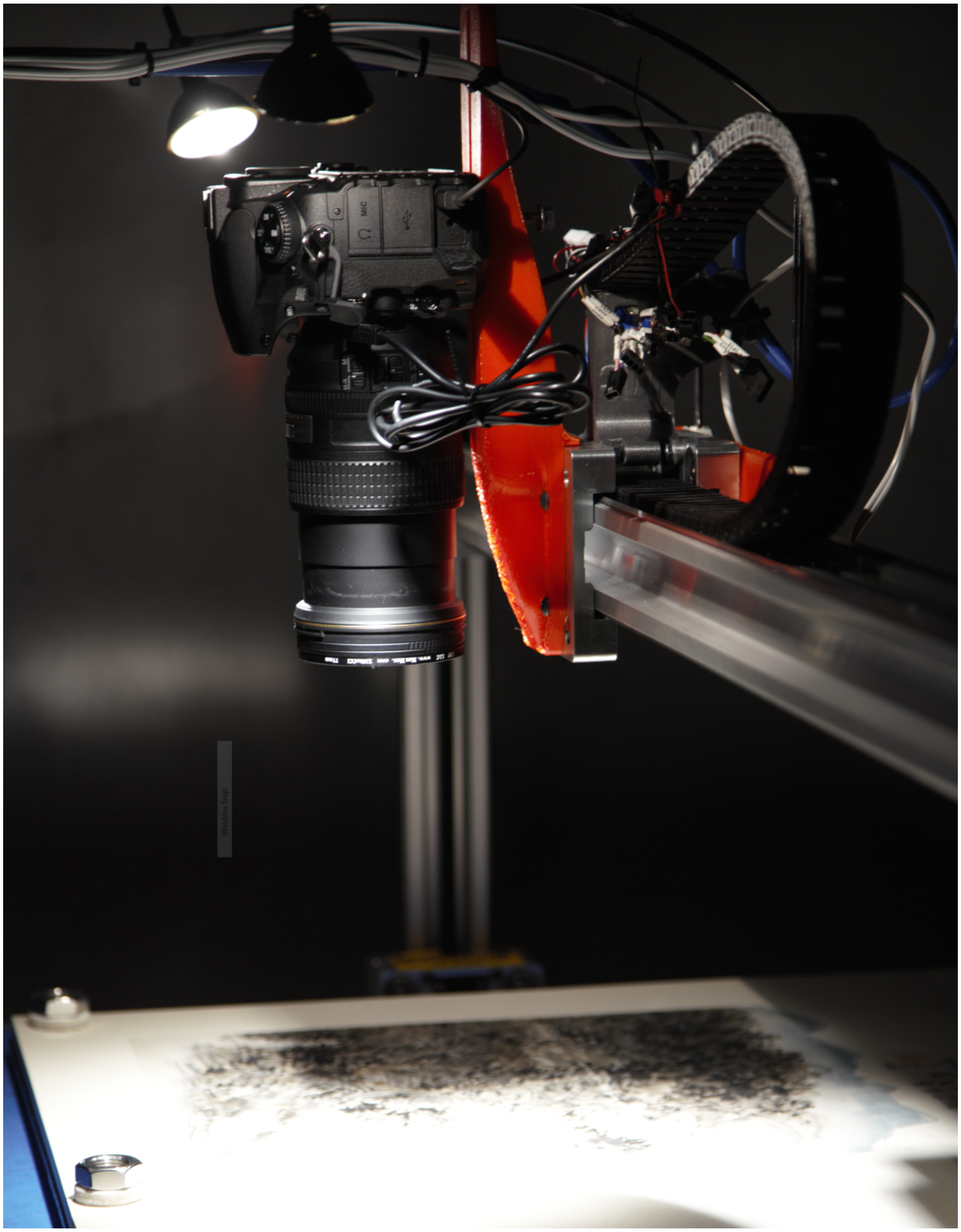

Figure 5.6. 3D Printed Camera and Lighting Mounts on WAVEcam: multi-axis robotic imaging platform.

Mosaic Path Planning The motion stage accepts standard g-code commands for CNC motion through either a serial port or by reading pre-programmed imaging paths off of an SD card. With this freedom and ease of control, an in-house a path planner was developed in the MATLAB environment to provide both the user interface and g-code generation. The process of constructing an imaging path takes 5 steps.

- First, after mounting the desired camera and lens, we measure the size of the frame taken by the camera at the imaging surface. This is done simply by photographing a ruler as accuracy to within a couple of millimeters is all that is necessary.

- Next the painting is placed on the imaging surface and plot out both the XY position of all four corners of the painting, as well as the camera height that focuses the painting in the exact center of the frame. These measurements are all recorded in the coordinates of the motion stage as the user manually moves the stage over a serial connection.

- The next step is to record the camera height which focuses the exact center and the exact corners of the frame in the center of the painting. This is covered in more detail in the next section.

- With these measurements recorded, the path planner generates a series of back and forth image locations in the X and Y directions across the painting surface knowing the size of the frame being captures as well was the user-defined image overlap. An overlap ratio as high as 0.5 is usually unnecessary but will help to prevent by the image stitching software in regions of the painting with few features.

- Next, the height of the camera is determined for each location based on simple interpolation between the recorded focused heights at the corners and center. If more than one image is requested by the user at each location, the Field Curvature Compensation method is used.

- Finally, the path planner generates a new g-code file along with a time estimate for completion. Even thought he system can be paused and resumed, the ability to predict the completion time helps drastically in the real world when planning a closed room with a strictly controlled lighting environment.

Key Specifications

The WAVEcam improves upon the traditional user experience of a heritage practitioner completing imaging and analytical exams on a work of art due to its precision, automation capabilities, faster workflow, and ease of use. WAVEcam has been designed to be customizable and is therefore able to be implemented with the user's current set of equipment. 3D printing of custom mounting brackets allows new sensors to be integrated into the workflow as these technologies continue to improve.

To achieve co-registered images in the infrared and visible bands, the user typically switches out the filters each time the camera is positioned and then re-positioned to achieve perfectly overlapping shots [11]. Since the WAVEcam is programmed to return to the same exact coordinates for each imaging run, it must only be ensured that the artifact does not move, and the filter setup can be swapped only once. Traditionally, the practitioner must invest a considerable amount of time towards the setup of equipment, including the positioning of the artwork, lights and tripod, and the exchange of filters. With the WAVEcam ultra-high resolution imaging platform the mount head co-locates both the sensor and illumination source, and is moved within a coordinate system controlled by g-code.

Since the factors like image overlap, shots taken, coordinates, and field of view can all be pre-programmed into the setup, the user is involved just once at the beginning.

The run times of the imager case studies described here are comparatively short, just nine minutes to acquire 20um pixels. The largest image captured which focused-stacked 5 images in each of 364 locations, took 143 minutes, this resolution was likely unattainable with the traditional setup especially within the new time frame. In addition, while the scan is running, the user has the ability to complete other tasks, since WAVEcam runs autonomously. The WAVEcam offers considerable user experience improvements over more traditional setups, such as [53] and [54].

5.1.3 Case Study: Huang Binhong watercolors

Implementation of Exam Methodology

The WAVEcam has been designed to follow the method previously described [4] and [61], for the technical photography of paintings. Additional references were also consulted to inform the workflow [11], [62]. The camera has been modified from its off the shelf state to have the internal infrared filter removed, thus making the CMOS sensor sensitive to 1100nm [34]. A selection of bandpass filters allowed for the various waveband imaging modalities to be captured [4]. An abridged selection of TP images was chosen based on the lighting scenarios and filters involved, to accommodate the time constraints we had while working with these rare artifacts. The paintings by Huang Binhong presented in this case study were sufficiently flat on the imaging bed to acquire images without the use of the biquadratic curvature compensation tool.

Post-processing Workflow Once the images are captured, they need to be combined to create one coherent high resolution image of the scanned artifact. First, the images at different heights for each (x,y) position need to be combined through focus stacking in order to increase the depth of field for the photos. This can be done manually through photo merging in Adobe Photoshop, or batch processed in Zerene

Stacker. The focus stacked images can then be stitched using commercial software, such as Microsoft's Image Composite Editor, which can stitch images with planar motion. The stitched image can then be converted into a tiled, pyramidal TIFF for real-time, high-resolution interaction in our visualization environments.

With a fully automated workflow, intervention from a human operator is minimized to just loading and briefly inspecting the data, allowing the computer to work independently. On our 8-core Xeon processing computer, the longest step of stitching 364 images for a total size of 6 gigapixels took less than 12 hours. Stitching, as described in [63], is not without error, and future research efforts will be directed towards the optimization and accuracy of this step.

Results of XRF Spectroscopy

Analytical diagnostic exams, such as point-based spectroscopy, can be carried out on the artifact simply by designing and printing a custom mounting bracket for a portable instrument. In the case of this study we have demonstrated this using an X-ray Fluorescence spectrometer (Bruker III-SD, Kennewick, WA)

Following the guidance of a careful reading of the multispectral images, as demonstrated in [33], areas were chosen for analysis by XRF. The unit was operated in non-contact mode and positioned manually to be fixed at 1mm over the intended spot of analysis (measuring 3x4mm). XRF is a complementary technique to technical photography because it provides elemental information about the sample, detecting elements from Si-Pb by atomic number. Organic materials containing primarily lower weight elements like C, N, H, F, and O cannot be detected. Nevertheless, we were able to obtain important information about the watercolor paintings.

The signature stamp shown in figure 5.5, was analyzed by XRF and determined to be cinnabar, HgS, based on the resulting spectrum, figure 5.7. The blue shirt of the

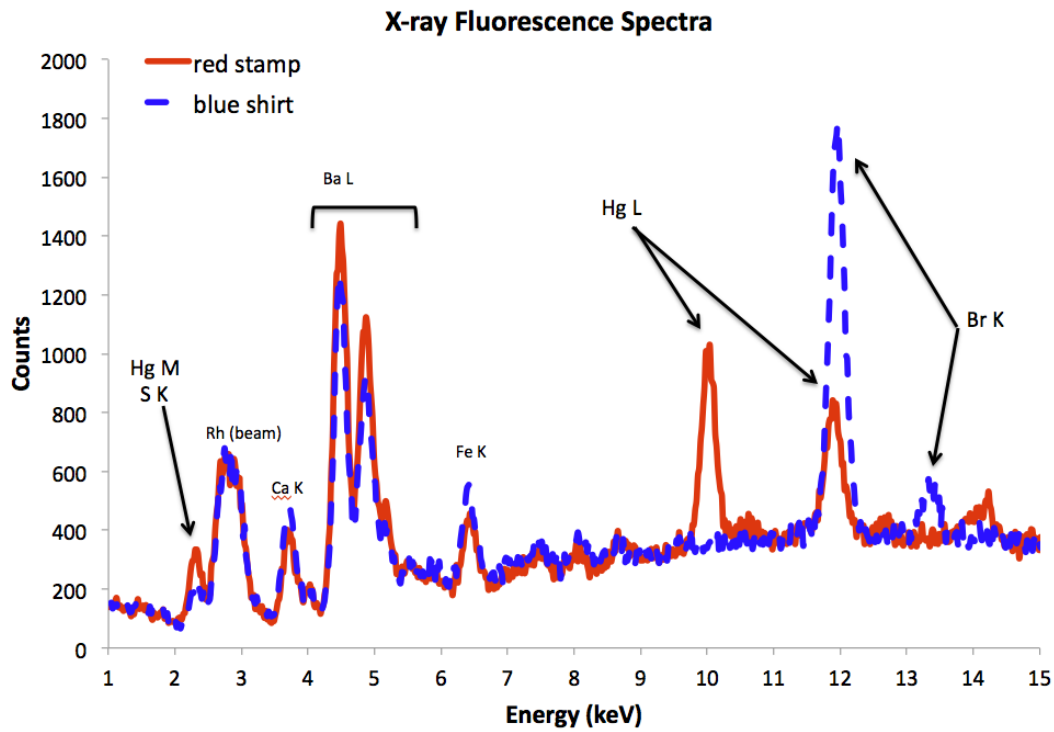

Figure 5.7. XRF spectra of two selected points of analysis. Solid line showing presence of Mercury, dashed line reveals the presence of Bromine.

small man was found to contain Bromine, and likely represents a common blue dye. Alternatively, most pigments in the body of the composition (black, red, green) resulted in spectra which did not evidence any particular element that would point towards a specific pigment assignment. However, signal corresponding to the element Barium was detected throughout the work, suggesting that a wash containing a Barium mineral was used.

User Experience Comparison

The WAVEcam improves upon the traditional user experience of a heritage practitioner completing imaging and analytical exams on a work of art due to its precision, automation capabilities, faster workflow, and ease of use. WAVEcam has been designed to be customizable and is therefore able to be implemented with the user's current set of equipment. 3D printing of custom mounting brackets allows new sensors to be integrated into the workflow as these technologies continue to improve.

Precision To achieve co-registered images in the infrared and visible bands, the user typically switches out the filters each time the camera is positioned and then re-positioned to achieve perfectly overlapping shots [11]. Since the WAVEcam is programmed to return to the same exact coordinates for each imaging run, it must only be ensured that the artifact does not move, and the filter setup can be swapped only once.

User Committed Time Traditionally, the practitioner must invest a considerable amount of time towards the setup of equipment, including the positioning of the artwork, lights and tripod, and the exchange of filters. With the WAVEcam ultra-high resolution imaging platform the mount head co-locates both the sensor and illumination source, and is moved within a coordinate system controlled by g-code. Since the factors like image overlap, shots taken, coordinates, and field of view can all be pre-programmed into the setup, the user is involved just once at the beginning. The run times of the imager case studies described here are comparatively short, just nine minutes to acquire 20um pixels. The largest image captured which focused-stacked 5 images in each of 364 locations, took 143 minutes, however, this resolution is likely unattainable with the traditional setup. In addition, while the scan is running, the user has the ability to complete other tasks, since WAVEcam runs autonomously. We believe the WAVEcam offers considerable user experience improvements over more traditional setups, such as [54] and [53].

Conclusions

The WAVEcam is a robust ultra-high resolution imaging platform uniquely adapted to acquiring images for wide-angle visualization environments. It has been designed to automate and accelerate the workflow for technical photography and spectroscopy in the digital documentation of relatively planar cultural heritage artifacts, like paintings and manuscripts. The imaging platform allows for customized usage scenarios through the ability to design and fabricate mounting brackets based on need. This case-study has demonstrated the capabilities and improvements of the WAVEcam, and we have shown enhancements of the typical workflow, including speed, resolution, and user obligation through the implementation of technical photography (acquiring multispectral mosaic images), and x-ray fluorescence point-based spectroscopy on paintings by Huang Binhong. There is room for growth and further implementation of more features and automation of the typical imaging and analytical diagnostics workflow, and we intend to continue development to this effect.

5.2 ARtifact Conservation - Augmented Reality Tablet Platform

This section presents an augmented-reality technique for the visualization of diagnostic imaging and analytical diagnostics data, creating a contextualized data analysis workflow. A mobile device with see-through video serves as the interface that intuitively combines the physical artifact with multispectral imaging and spectroscopy data, strengthening the analytical process carried out during conservation efforts. An improved workflow for the acquisition of point-based X-ray Fluorescence (XRF) spectra is proposed and demonstrated, using the sensing capabilities of the mobile device. The presented, contextualized data analytics approach enhances the retention of important metadata, while streamlining the collection and comparison of key datasets routinely used for material identification.

Figure 5.8. Portable XRF instrument supported by a tripod, shown here scanning one point on the Sicilian Cart.

5.2.1 Tool Development and Preliminary User-Experience Study

Introduction

X-ray fluorescence (XRF) spectroscopy has become an important technique and tool, used by researchers studying cultural artifacts. The non-destructive nature of XRF analysis, swift setup, short acquisition times, and ease of use make it a desirable and preferred instrument from a conservation standpoint, encouraging broad adoption by heritage conservation practitioners [64, 65, 66]. In particular, handheld, portable XRF instruments, which can be easily transported and deployed under most field scenarios and conditions [19], are now widely used for fieldwork.

Section 3.1 described the procedural workflow for the assessment of a work of art. According to the methodology previously presented, a diagnostic imaging survey (TP) is commonly performed first, followed by an XRF study carried out on selected

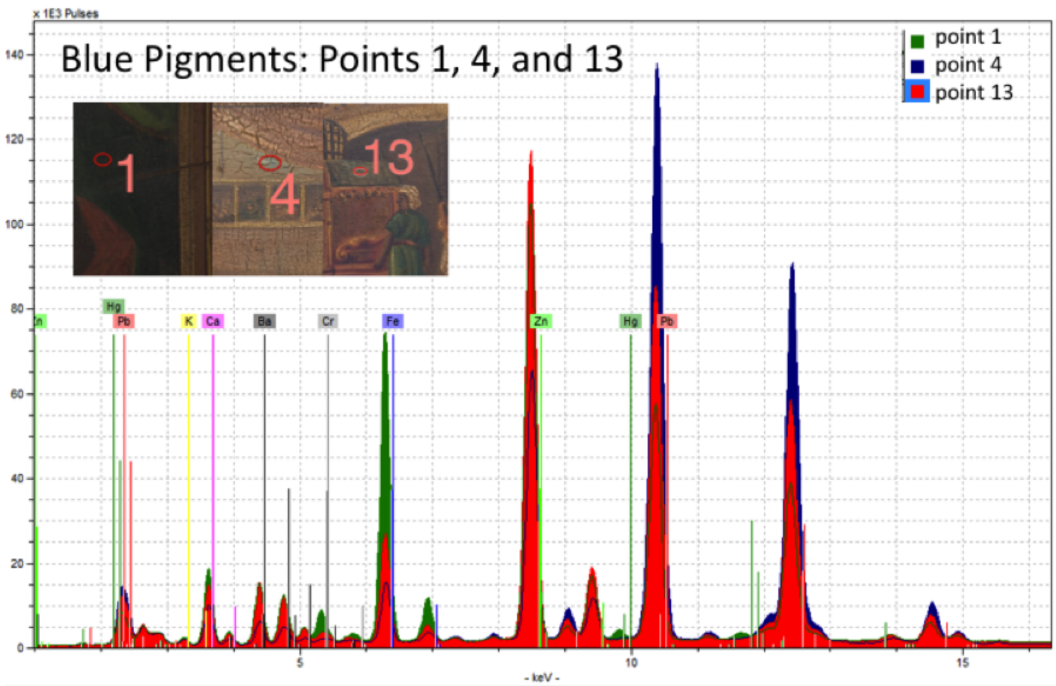

Figure 5.9. Example of data overlay using multiple platforms, constructed manually using the methodology employed previously.

points, based on the careful interpretation of the imaging data. While the combination of multispectral and spectroscopic data can provide invaluable insights about an artifact, existing visualization techniques for this type of data typically create a disconnect between the data being analyzed and the physical artifact for which it was acquired. This forces the practitioner to either study only one modality or constantly shift between the physical and digital representation of the artifact. These context changes create multiple challenges in regards to data correlation and interpretation, requiring the user to refocus, reacquire features, and mentally map the digital representation back onto the physical artifact and vice versa. A solution to this analysis challenge was proposed by Vanoni et al. who introduced a contextualized visualization technique called ARtifact, using augmented reality to superimpose digital content directly onto physical artifacts [67].

ARtifact's augmented reality, video see-through interface allows the user to explore artifacts in-situ and maintain an artifact-centric analysis approach streamlining analysis and reducing cognitive load. One of the first capabilities explored with ARtifact was superimposing multispectral data onto artifacts, enabling the viewer to effectively see what cannot be seen and perform analysis directly on the artifact. The work presented here focuses on spectroscopic data and its seamless synthesis and visualization alongside high-resolution multispectral data, providing an integrated workflow for acquiring and analyzing artifact-related information. The presented workflow supports deep space-time exploration, allowing the state of the physical artifact and its digital representation to be recorded and visualized over time, thereby creating the equivalent of a "digital clinical chart" (Section 2.1.1) capturing the artifacts state of health and state of conservation. Since all data are contextualized, the data analysis workflow itself can be recorded and replayed, resumed, or continued at any given time by simply aiming the mobile device at the artifact. A case study demonstrating the contextualized visualization methodology is presented for a painted wood panel of a historic Sicilian cart (Fig. 5.8), dating from the 1920's and belonging to the collection of master Domenico Di Mauro, a 101-year-old traditional Sicilian cart painter in Aci Sant'Antonio, Sicily.

ARtifact Contextualized Visualization Approach

ARtifact utilizes a technique known as video see-through augmented reality (AR) in which virtual objects are superimposed in real time onto a live video stream captured with the rear-facing camera available on most of todays mobile devices, including smartphones and tablets. The video is captured and each video frame analyzed for the existence of a known artifact for which additional data is available. If a known artifact is found, it is flagged, subsequently continuously tracked, and available data augmented on top of the video, based on user definable filters. This means that contextualized data visualization becomes as easy as pointing the mobile device at the physical artifact.

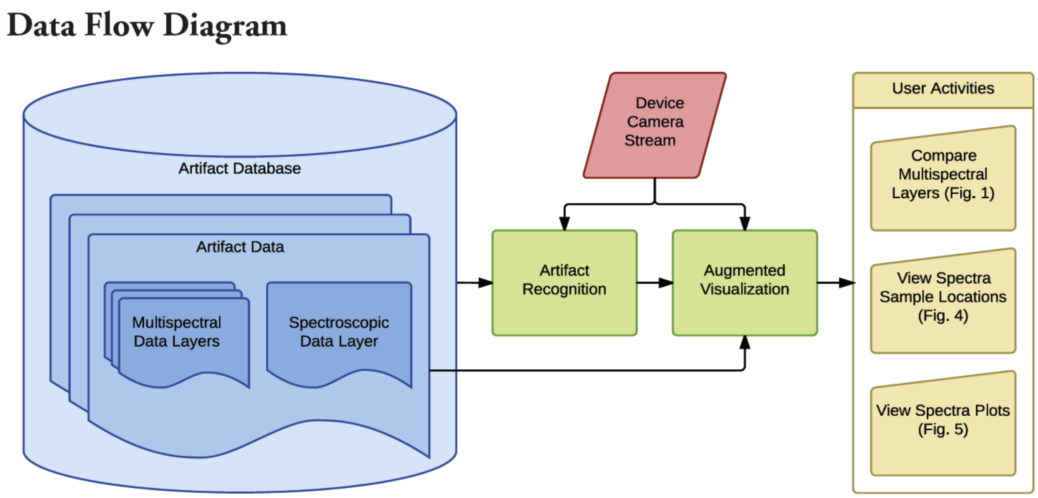

Figure 5.10. Data flow diagram showing the design of the ARtifact tablet platform

Tablet devices with their larger, high-resolution, multi-touch screens, powerful processors, and mega-pixel resolution cameras are particularly attractive for this data visualization approach and are used as the primary interface for the presented work.

Technical Approach

In order to superimpose artifact-related data in the correct screen location when looking at an artifact, the tablet must determine its position and orientation (pose) relative to the artifact. This is accomplished via real-time feature tracking of textured planar targets [68], enabling direct tracking of artifacts such as paintings without the need for any additional fiducial markers. By specifying the real-world dimensions of the artifact, ARtifact can perform digital distance measurements and properly scale on-screen overlays such as spectroscopy sample points.

The initial version of ARtifact enabled intuitive interaction techniques for analysis and comparison of multispectral data layers. Any of the available layers can be superimposed on top of the live view of the artifact, providing a sort of "magic lens" that alters the viewer's perception of the artifact. An on-screen slider allows for varying the

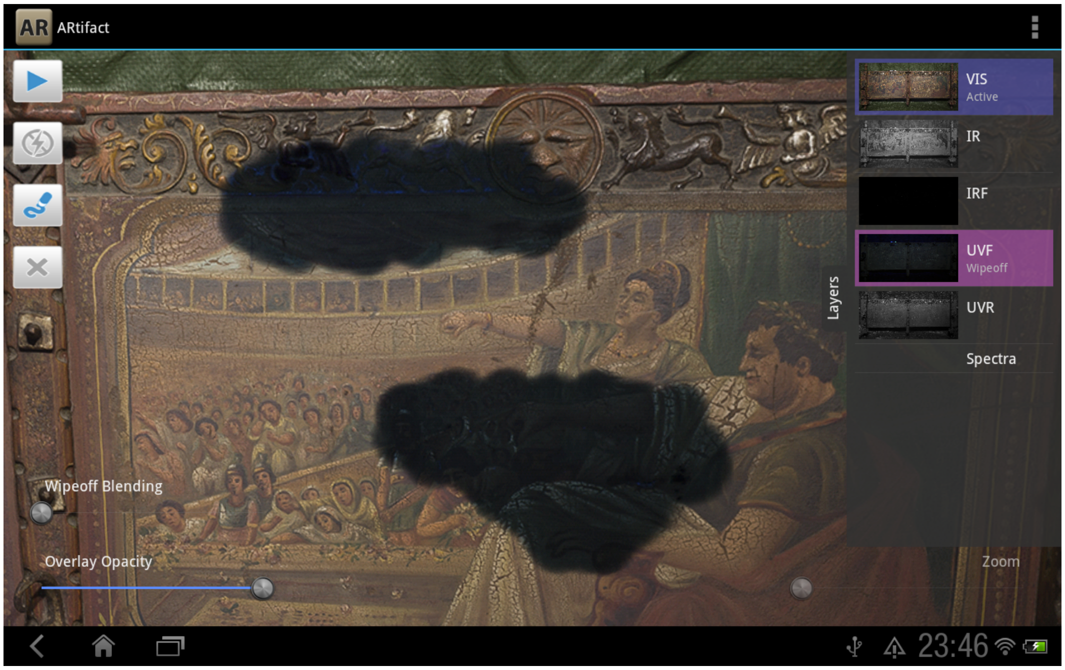

Figure 5.11. "Wipe-off" comparison of visible (VIS) image with ultraviolet fluorescence (UVF) image.

opacity of the overlay for comparison of the data layer with the actual artifact. The user can get a better view of the data by using the well-known pan and zoom multi-touch gestures or by simply moving closer to the artifact. For more refined comparison between layers, ARtifact also provides a "wipe-off" mode that gives users the ability to wipe off one layer with their fingers to reveal another (Fig. 5.11). This technique enables targeted investigation of a region of interest without modifying the surrounding data, providing context for the wiped area.

Integrating Spectroscopic Data

Spectroscopic data can now be accommodated within the ARtifact augmented reality application. Initial development focused on loading and visualizing XRF data. The spectra are transferred to the tablet in their raw form as CSV or TXT files and associated with the desired artifact. The real-world location of the sample point on the artifact is also specified, based on a photo taken from the devices built in camera. With this user-supplied information, ARtifact is able to superimpose circular indicators on the artifact to map each of the sample points acquired (Fig. 5.12). When the user taps one of these indicators, the spectrum data for that point is loaded and displayed on a graph (Fig. 5.13).

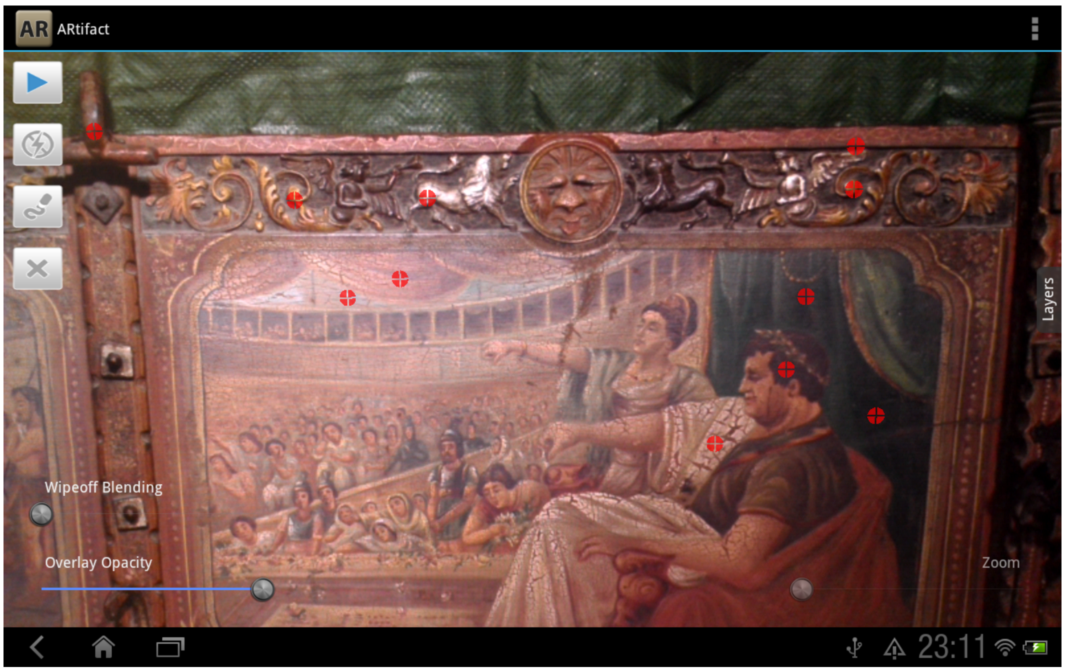

Figure 5.12. Augmented reality overlay showing points where spectral data was collected.

Operational Methodology for Point-Based Spectral Datasets

When using a handheld, portable XRF instrument to collect discrete point samples, care must be taken to retain all metadata associated with each site. This typically includes the precise location and size of the spot analyzed, the visual appearance or color of the spot, and the users motivation for choosing that spot. The latter is usually based on the reading and interpretation of the multispectral dataset itself, comparing several images to notice critical differences and unique markers. By harnessing the multispectral image

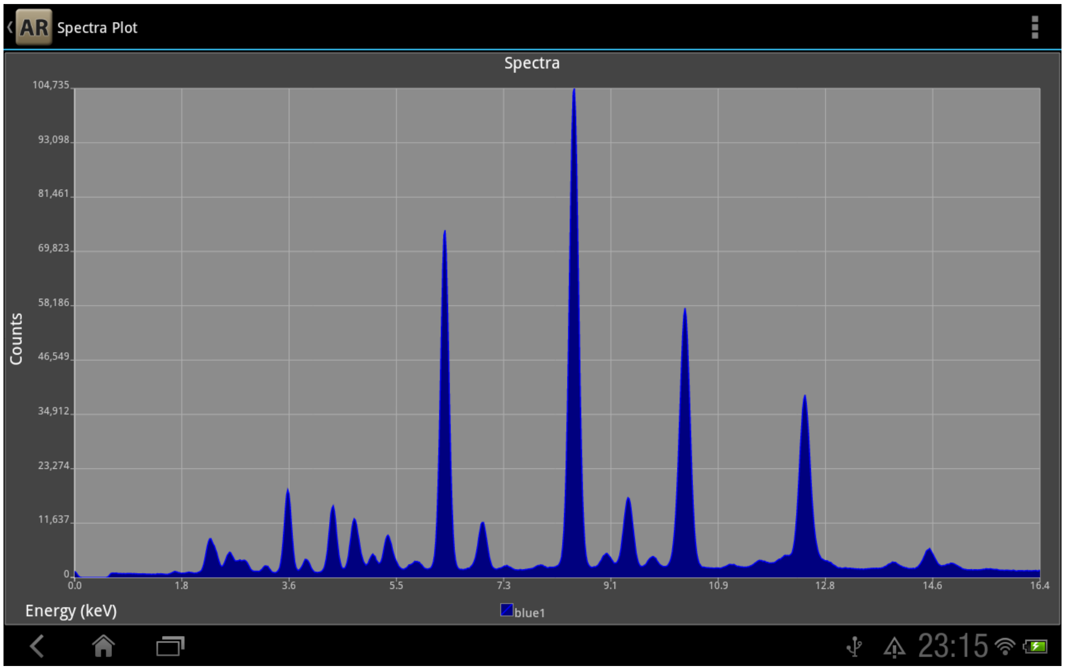

Figure 5.13. Plot of XRF spectrum for blue pigment sample visualized in-app.

data for informed data collection and contextualized visualization, it is possible to create a powerful, optimized workflow. Using the tablet in tandem with a handheld XRF, the user first scans and evaluates the multispectral images, making use of the wipe-off mode to choose the target areas that should be further analyzed with XRF. Once the target areas have been identified, the user can simply annotate them by drawing circles of the relevant spot size, marking the area or point to be studied. Following the pre-selected map of points to be analyzed, the user can easily co-locate their physical location on the artifact and position the handheld instrument to collect the spectrum. ARtifact will prompt the user to name each spot and the user would give the same name to the spectral data file. With just a simple file transfer the spectra are then available for viewing and annotation in-app.

Case Study: Sicilian Painted Wooden Cart Panel, c. 1920, Aci SantAntonio

The Sicilian cart is an ornate and colorful wooden cart drawn by a horse or donkey, native to the island of Sicily. Aci SantAntonio played a pivotal role in the development of this fashion, since it was the location of painting workshops specialized in the decoration of the carts. The other important workshops were in Palermo and Agrigento, serving the cart production on Western side of the island. The workshops of the east and west developed different artistic styles, motifs, and colors. The Museum of the Sicilian Cart in Aci SantAntonio, Italy has just opened recently in 2014, and the small local nature of the museum means that the artifacts typically would not have the opportunity to undergo scientific analysis by a conservation team, as is standard in larger museums. The collaboration between our research team and this museum represents the first scientific examination on this type of art. The artifact chosen as the subject of our case study is a painted wooden panel from a traditional Sicilian cart, dating back to the 1920's. We have chosen to study this artifact because it is one of the oldest pieces that still presents the original painted layer. Most of the other pieces have been heavily retouched or entirely repainted over the years. The current state of conservation of the panel is fair. It presents some paint cracks from decades of exposure to humidity and temperature change, causing expansion and contraction of the painted layer. The painted surface has been covered with a protective varnish that has yellowed slightly, however, there are no paint delaminations, so the piece is stable enough for analysis and does not require preventative intervention.

We analyzed 18 spots with a portable, handheld XRF instrument, a Bruker Tracer III-SD, with the experimental procedure following that of previously published work [6]. The goal of the analytical survey was to characterize the palette of pigments used by the artist, and to confirm the presence of original material, avoiding pigments manufactured

Figure 5.14. Sicilian cart: Map of spots analyzed with portable XRF.

post the 1920's era. The combination of multispectral imaging with XRF, provides an initial data scaffold for the development of a comprehensive analysis plan and preliminary data for pigment identification.

Results ARtifact provides an agile platform for the collection and retention of diagnostic data important to the assessment of the state of conservation of cultural artifacts, while affording the user the ability to view and interact with these datasets in a contextualized manner through augmented reality. The proposed methodology using augmented reality to read and manipulate multispectral imaging datasets, blending different modes and annotating the images, and designing a plan for the XRF analysis, makes full use of the complementary nature of these two diagnostic techniques. Since these diagnostic exams are accessible, non-destructive, and often the first analyses employed to assess a work of art, it is important that their synergy be maximized. We find that the co-location of the datasets within ARtifact increases the users ability to retain critical metadata that accompany the spectra, and combine it with key insights based on individual user expertise. ARtifact has been designed to facilitate a methodological

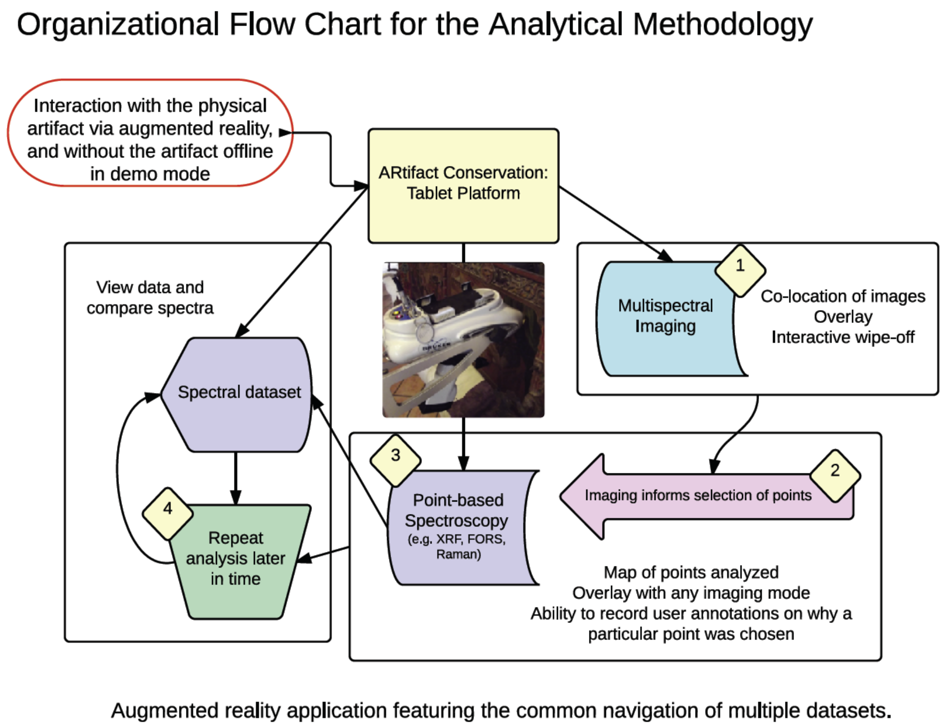

Figure 5.15. Organizational flowchart for the analytical methodology enabled by the ARtifact tablet application.

workflow for practicing field researchers in both multispectral imaging and XRF of cultural artifacts. Since ARtifact provides a contextualized baseline record, it implicitly also creates an imaging plan for follow-up XRF exams, allowing results to be easily compared and changes tracked over time, establishing a dynamic record of the state of conservation of the artifact.

In our case study, a technical photography was carried out, capturing images of the panel in the ultraviolet, visible, and infrared ranges of the spectrum, as well as a false color infrared (IRFC). In the infrared reflectography mode (IRR, 0.9-1.7um wavelength) the multispectral imaging survey revealed an extensive underdrawing, which, when rendered in ARtifact, supports direct comparison to the visible layer above. The IRFC image helps to distinguish pigments presenting the same visible color that have different infrared transparencies, such as red ochre and vermilion. The UV fluorescence image reveals the state of the varnish layer.

The XRF survey of 18 spots, focused on characterizing the artist's palette, also revealed some insights into the working style of the artist. A strong presence of characteristic lines corresponding to lead in all of the spectra indicate that the pigment lead white was used extensively to lighten pigment colors. Additionally, in some white and lighter regions studied, we also observe the presence of barium and zinc, indicating the use of lithopone white. This is especially observed in areas painted a darker color blue, where we did not detect the presence of any elements corresponding to the blue colored pigment. This transparency allowed for higher sensitivity to the deeper ground layer, likely painted with lithopone. It was also demonstrated that the blue color is made of lightweight elements or organic material, not detectable with XRF. Two reds were observed, both through MSI and confirmed with XRF, red ochre (Fe_2O_3) with strong iron content, and vermilion (HgS), displaying peaks from mercury and sulfur. The yellow pigment was identified as chrome yellow ($PbCrO_4$) through the observation of strong peaks from both chromium and lead in the points studied. Additionally, green areas were found to exhibit chromium peaks, suggesting that the green was a mixture of yellow and blue pigments. The results from the brown areas studied are also in accordance with this assumption, given that the spectra show key characteristics of the red, yellow, and blue pigments used elsewhere on the panel. Although, due to the complex nature of the painted surface and the limitations of the technique, all of the pigments cannot be confirmed, but we can make the proposition that the Sicilian cart painter likely used only the primary colors plus two types of white paint for his palette. Elements that would be indicative of materials from a later era, such as titanium (titanium white), were not detected.

Conclusions

Augmented reality holds great promise for the creation of a new data-driven acquisition and diagnostics workflow, where different imaging and sensing techniques inform each other. An improved workflow for the acquisition and visualization of point-based X-ray Fluorescence (XRF) spectra was presented, using the sensing capabilities of a tablet device to create a contextualized data analysis workflow and augment digital data directly onto physical artifacts. This contextualized data analytics approach enhances the retention of important metadata, while streamlining the collection and comparison of key datasets routinely used for material identification. The technique for spectra acquisition and visualization can be broadly applied to other spectroscopy techniques typically applied in non-invasive investigation of cultural artifacts, such as fiber optics reflectance spectroscopy (FORS) [69] used in the field to study art [6].

5.2.2 Case Study Summary

ARtifact was designed specifically to support the diagnostic exam methodology based off TP and XRF being developed in this dissertation work. The first test case confirmed the potential of the application as an easy-to-use platform to integrate the two datasets. The choice of a tablet application allowed the goal of maximum portability to be preserved. For example, ARtifact could be used just as well high up on a scaffold with no access to power in front of a mural painting in fact, that is where one may want to use it the most!

The important concept to note from this chapter is that software and data storage and visualization tools need to be developed in an interdisciplinary environment where researchers with the appropriate expertise can work together to build custom designed solutions. It is pertinent to tailor the data scaffold to the methodological procedure and not vice versa. There are many technological and software tools that can improve and support the user's workflow.

Chapter 5, in part, is a reprint of the material as it appears in D. Vanoni, S. Stout, A. Cosentino. "ARtifact Conservation: Representation and Analysis of Spectroscopic and Multispectral Imaging Data Using Augmented Reality" Proceedings of the 18th ICOMOS Meeting, Track 5: Emerging Tools in Conservation Science. Florence Italy, (2014). The dissertation author was a primary investigator and author of this paper. Chapter 5, in part, has been submitted for publication of the material as it may appear in the conference proceedings of Digital Heritage 2015: S. Stout, J. Strawson, E. Lo, F. Kuester. The WAVEcam: Ultra-high Resolution Imaging of Paintings Digital Heritage 2015, Granada, Spain. The dissertation author was the primary investigator and author of this paper.

Chapter 6

Evaluation of the Technique: Investigations on Method Performance and Limitations

Two investigations were undertaken to explore the performance of the chemical imaging methodology of the diagnostic exam, to test the accuracy and identify scenarios producing weak performance or potentially confusing results. This methodology was developed based upon the expertise and insight gained during practical experience from the case studies described in Chapter 4, where the initial versions of the diagnostic exam were applied for pigment identification in the field.

The first study was performed on a mock-up painting of a Madonna and Child crafted by students at the Pratt Institute. This painting has already undergone technical study as part of the multispectral imaging work presented by [7], where the technique and materials used to execute it are also described in more detail. Here the XRF analysis will be added to the existing work, and the results will be presented and discussed along with an evaluation of the effectiveness of the methodology.

The second study was carried out on a series of paintouts prepared in attempt to create paint mixtures and painted layers that would be more complex than the single swatches of the pigments checker, and therefore, produce datasets that begin to approach those of an actual painting scenario. The intention is that these new datasets will help to better define the limitations of the diagnostic exam not just in terms of fundamental detection capabilities of the instruments and techniques used, but also in terms of specific material characteristics of the pigments themselves relative to their position as part of a work of art. An adapted flowchart method, described in Section 3.3, was chosen as a conduit for the data processing and interpretation of the results because it aligned with the philosophy and approach of the methodology as an accessible and low-cost solution that would perform reliably in a standardized way.

6.1 Case Study: Painting Scenario - Pratt Madonna

6.1.1 Introduction

The Pratt Madonna is a mock-up of a Renaissance painting executed with historical and modern pigments in order to simulate a painting that has been heavily restored and retouched [7]. It was developed as an analytical aid and teaching tool at the Pratt Institute. The sky was painted partly in ultramarine and partly in azurite. Three different green pigments were applied on the background: verdigris, malachite, and chrome green. The shirt was painted with red ochre mixed with lead white, though the right sleeve was painted with cadmium red. Lead white was used as a lightening agent, though the white brooch was made with titanium white.

Cosentino, is his paper on Multispectral Imaging and the Art Expert, shows the image segmentation based on the multispectral imaging taken in 12 bands [7]. The study described here precedes that study and was undertaken to help evaluate the capabilities and synergy of the diagnostic exam for pigment identification using two techniques TP and XRF. Here the results will be presented and they can be compared to those of the recent paper [7].

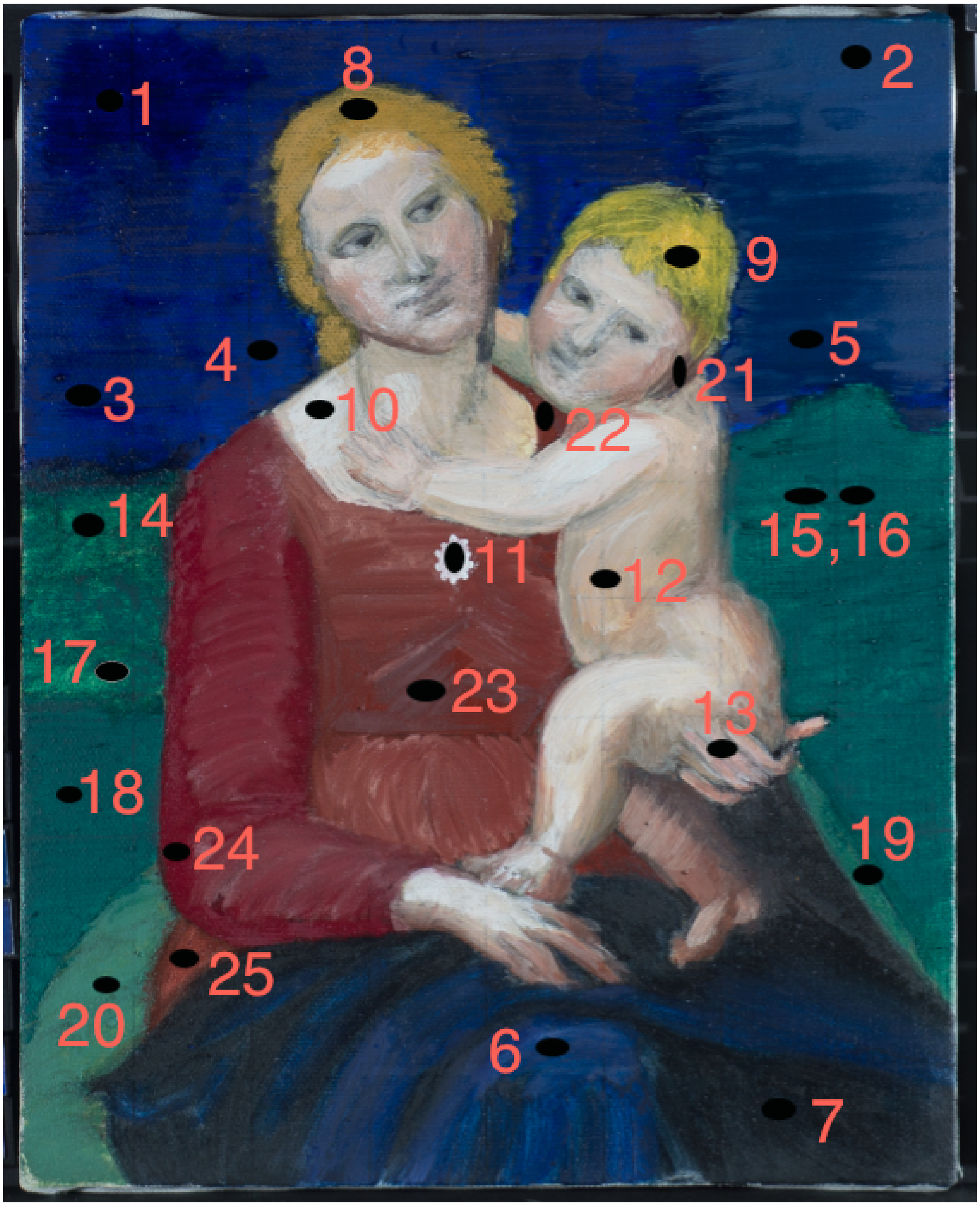

Figure 6.1. Pratt Madonna: map of spots analyzed with portable XRF.

6.1.2 Data and Analysis: TP and XRF

Technical Photography

Technical photography was taken according to [7], also following the recommendations in the diagnostic exam.

Figure 6.2. Pratt Madonna: Visible light, with pigment swatches surrounding.

Figure 6.3. Technical Photography of the Pratt Madonna surrounded by pigment swatches: a) VIS, b) UVR, c) IR, d) IRFC.

X-ray Fluorescence Spectroscopy

XRF spectra were collected consecutively according to visible color observed. Therefore, points 1-7 appear blue, points 8 and 9 yellow, points 10-13 are white, points 14-20 are green, and points 21 to 25 are red (or a reddish mixture). Figure 6.1 shows the map of points analyzed and the spectra from each color group are shown in subsequent figures, (Fig. 6.4, Fig. 6.5). Differentiation between spectra from different pigments of the same color can be observed. The data were collected and processed according to the diagnostic exam procedure described in Chapter 3.

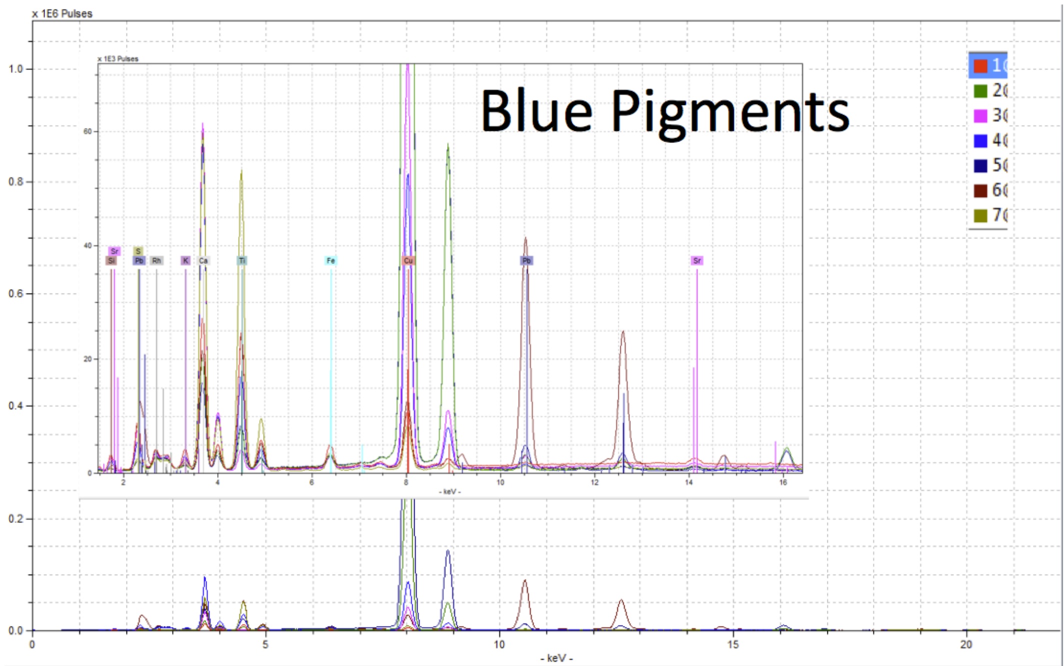

Figure 6.4. Pratt Madonna: spectra of blue areas analyzed with portable XRF.

6.1.3 Preliminary Results

The protocol for the diagnostic exam for the non-invasive identification of the artist's palette of pigments was carried out on the Pratt Madonna according to the steps described in Chapter 3. The data were put through both the MSI flowchart and the improved TP/XRF flowchart to arrive at the palette of pigments used by the artist. Using the full imaging suite successfully determined all of the pigments present. However, with only the 4 modalities chosen for the diagnostic exam, XRF was also necessary to positively identify all of the pigments present.

The case of the Pratt Madonna represents a mid-size painting scenario with a varied palette of pigments. As is apparent in the TP images, Fig. 6.3, several different

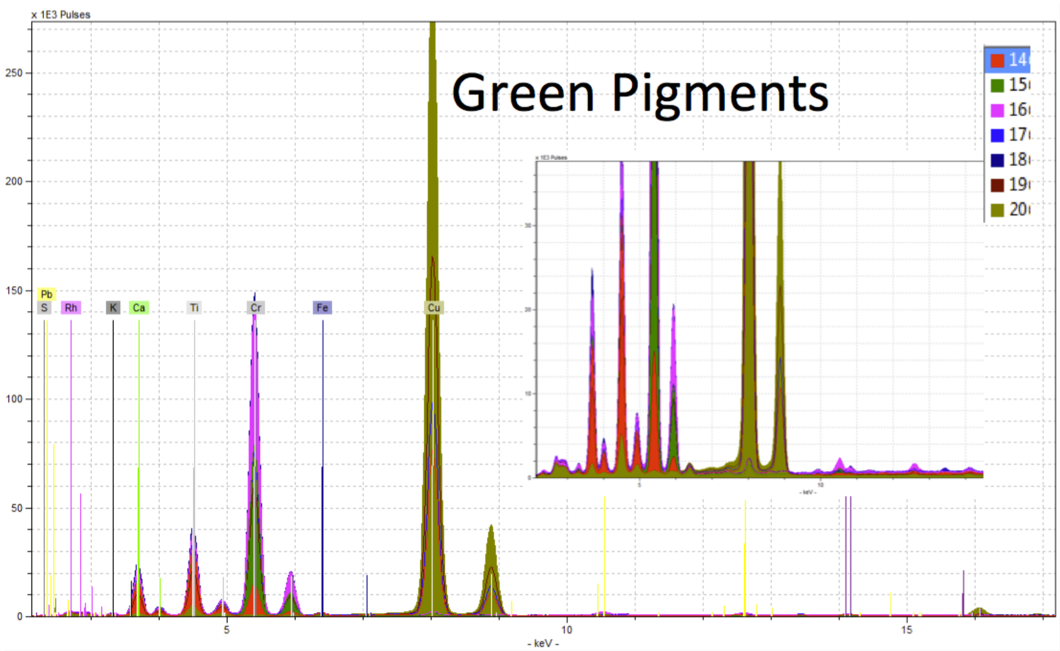

Figure 6.5. Pratt Madonna: spectra of green areas analyzed with portable XRF.

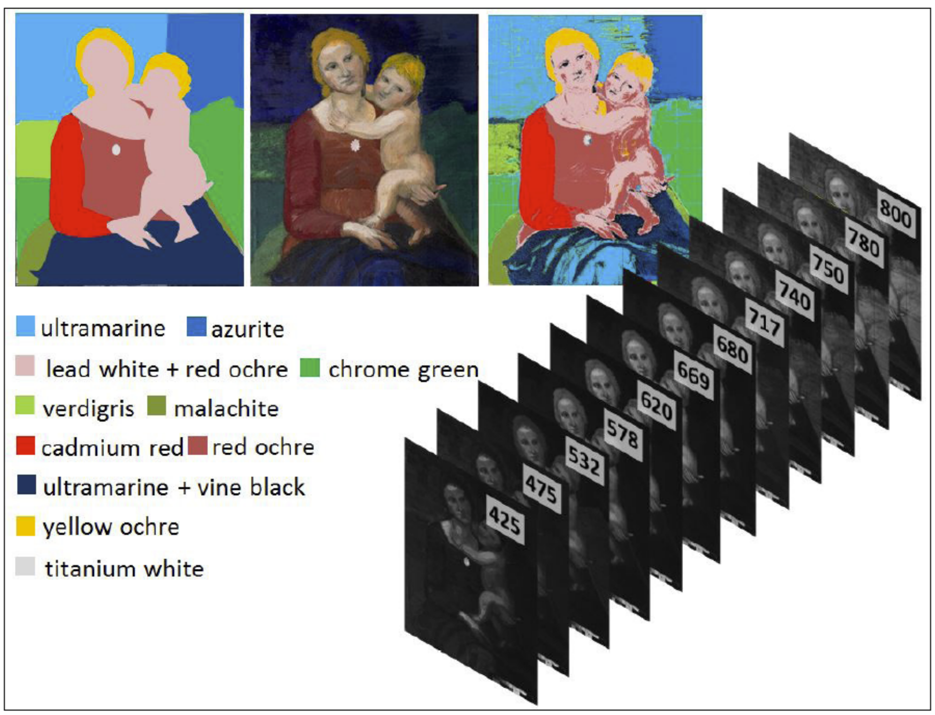

Figure 6.6. Pratt Madonna: results of multispectral imaging with 12 bandpass filters, from [7].

spectral responses are observed from eleven pigments in all. The diagnostic exam was successful in identifying the entire palette, however, the composition was fairly straightforward with well-segmented sections using only one pigment to cover the area. Figure 6.6 shows the image segmentation after multispectral analysis with 12 narrow bandpass filters. The far right inset image reveals areas where pigments have been mixed or used in the same area. The objective of identifying the "palette" with no strict obligation for highly specific mapping is sufficiently covered by applying the diagnostic exam as-is.

6.2 Case Study: Mixture and Layering Scenarios

In the scenario of a real painting, it is likely that the point analyzed will contain materials that cannot be detected, or cannot be definitively narrowed down with only the two analytical techniques employed in the chemical imaging methodology. An area using only one pigment is also rarely found, meaning that we must expect to encounter multiple materials, especially because the underlying layers (as shown previously, Fig. 2.5) can affect the results of the diagnostic exam to varying degrees. The purpose of this case study is to elucidate the extent of the degree by which the results obtained by the chemical imaging methodology can be manipulated or distorted by the nature of pigment mixtures or overlapping pigments. Most importantly, this study should evaluate in which type of scenario the method will fail, and ascertain the reason for the failure based on material properties and response to the analytical techniques.

Three separate collections of paintouts were prepared for testing based on a collection of twelve pigments chosen for analysis. The pigments were chosen to represent some ubiquitous materials and some hard cases to perhaps discern when mixed. More of the reasons will be noted in the discussion of the results. List of pigments: Lead Tin Yellow I, Lead Tin Yellow II, Azurite, Ultramarine, Phthalo Blue, Lapis Lazuli, Lac, Vermilion, Umber, Red Lead, Lead White, Zinc White and Titanium White.

The first collection represents the colored pigments mixed with white. Two series were made, one mixed with Lead White and one with Zinc White. The main goal was to explore the detection ability of the colored pigment with XRF in varying concentrations, while also having a visual reference to compare the TP response with the XRF data. Since colored pigments appear in paintings frequently mixed with white (or vice versa in the case of fleshtones), it is important to understand the intricacies of how the chemical imaging methodology performs in these scenarios.

The second collection represents binary layers of two pure pigments, one on top of the other, and is meant to get a sense of how transparencies and varying absorption characteristics can influence the perception and results when paints are layered. In one test plate, ten pigments are painted out in lines vertically and then crossed horizontally to make all the possible layering combinations. In the other test plate the white pigments were laid first as a ground layer with swatches of the colored pigments on top.

The layering scenario is a good test to see where the flowchart method may fail from an imaging standpoint, and also to discover when the XRF analysis may particularly help to arrive at a more accurate conclusion. The evaluation can also be performed in the reverse way, where potentially hard to interpret XRF spectra are aided from information gained through TP. The layered plates serve to assess the synergy of the two techniques and the robustness of the methodology, and document the circumstances for success and failure.

6.2.1 Preparation of Samples

Paper plates were chosen as the substrate for the test paintouts. They were cheap and available and did not produce a significant elemental addition to the XRF spectrum. Additionally, they worked well with the linseed oil paints because they allowed for

Figure 6.7. Tube paints used in the experiment.

sufficient absorption of the oil, which resulted in an adequate drying time suitable for the purpose of the experiment.

Pre-mixed tube paints in pure cold pressed linseed oil from Natural Pigments were used, unless stated otherwise. For pigments where a tube variety was not available, the ground pigment in powder form was mixed with pure cold pressed linseed oil. As oil absorption varies by pigment, oil was added dropwise until saturation was achieved: guidelines for absorption are sometimes listed in the manufacturer's pigment technical details. It must be stated that no attempt to further grind the pigments was made and that they were used in the form that they were received. The procedure for an artist would likely vary, as artists will grind and mix their own pigments. It was chosen to eliminate this step to avoid additional equipment and setup time.

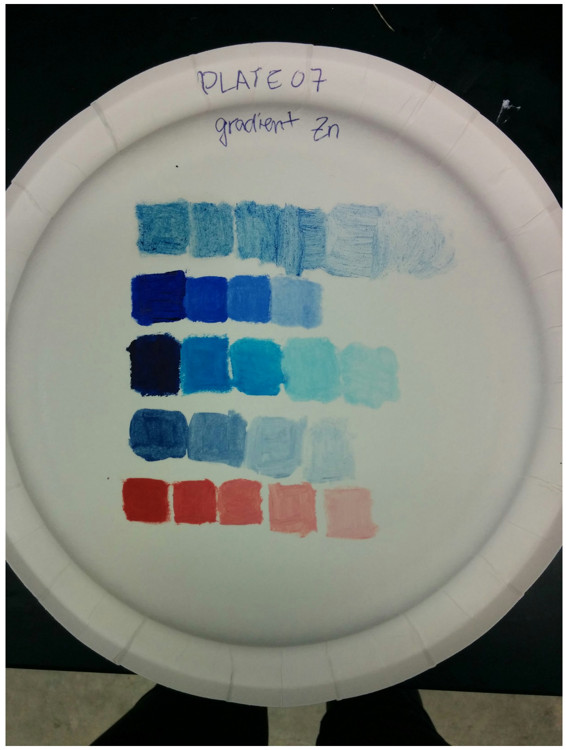

Figure 6.8. Example of a plate with paint gradient swatches, pure color shown with increasing Zinc White. (top to bottom: Azurite, Ultramarine, Phthalo Blue, Lapis Lazuli, Vermilion)

Paints were mixed up in small plastic cups making every attempt to attain a uniform mixture. For the first gradient mass percent was calculated by weighing the cup before and after the addition of pigment. The color was put in the cup first, and then the white was added. It clearly became apparent that mass percent gradient would be impractical to achieve due to the varying tinting strengths of the pigments chosen. A more practical gradient would be achieved by varying the appearance of the saturation/depth of color according to the human eye. The first series of weighed paintouts could then serve as a guideline to the approximate mass percentage, along with the XRF spectra, which would be roughly indicative of the quantity of each pigment present. It is acknowledged that a precise measurement of the quantity of each pigment would have been an ideal figure to obtain, yet proved to be too impractical.

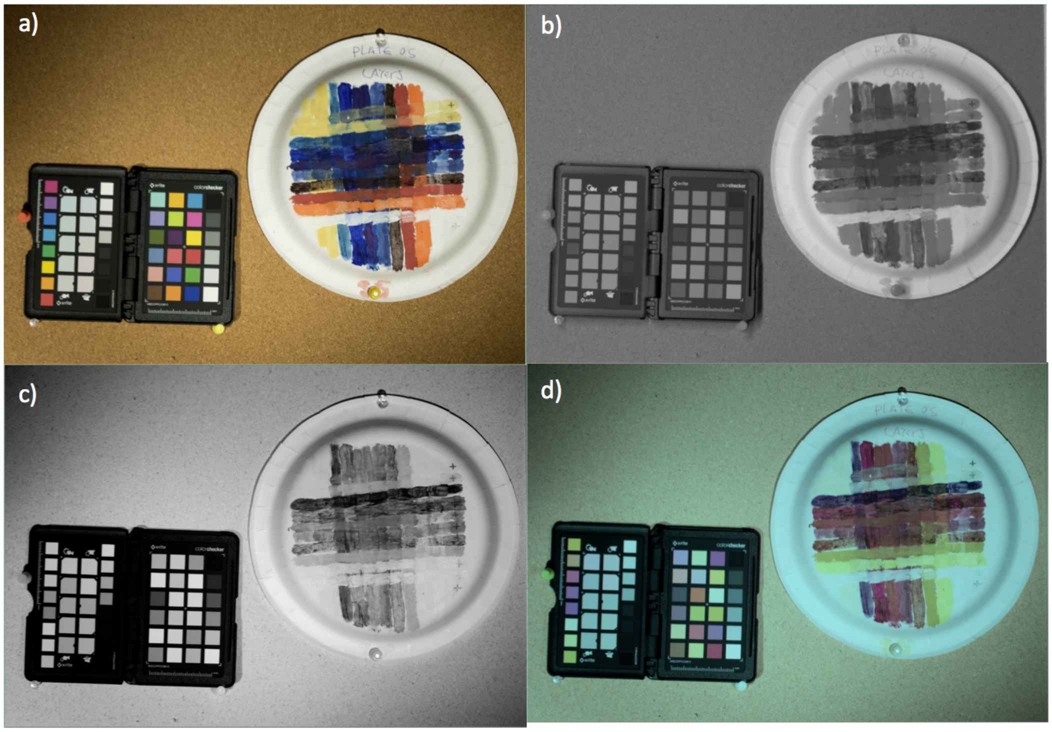

Figure 6.9. TP of Plate 5: Binary pigment layers. Pigments from L to R (Lead Tin Yellow I, Lead Tin Yellow II, Azurite, Ultramarine, Phthalo Blue, Lapis Lazuli, Lac, Vermilion, Red Lead, Lead White) a) VIS, b) UVR, c) IR d) IRFC.

For the gradient scenario three plates were painted. One with gradients of lead white in colored pigments, where the first swatch is pure color and white is added in increasing amounts; and the other where the same procedure is followed with zinc white. Each pigment responded to the addition of white in a different way and there was some difficulty in attaining visibly different swatches, or manipulating how much the color did change with just a small addition of white. Every best attempt was made to ensure comparable swatch samples that would serve the purpose of the study. Additionally, different brushes for each pigment were used to avoid contamination as much as possible.

For the layered sample plates the risk of contamination was greater than for the gradient plates. When wet paint is applied, even over dry paint, the existing paint layer can be re-wet and bleed across the surface and onto the brush. This is a characteristic

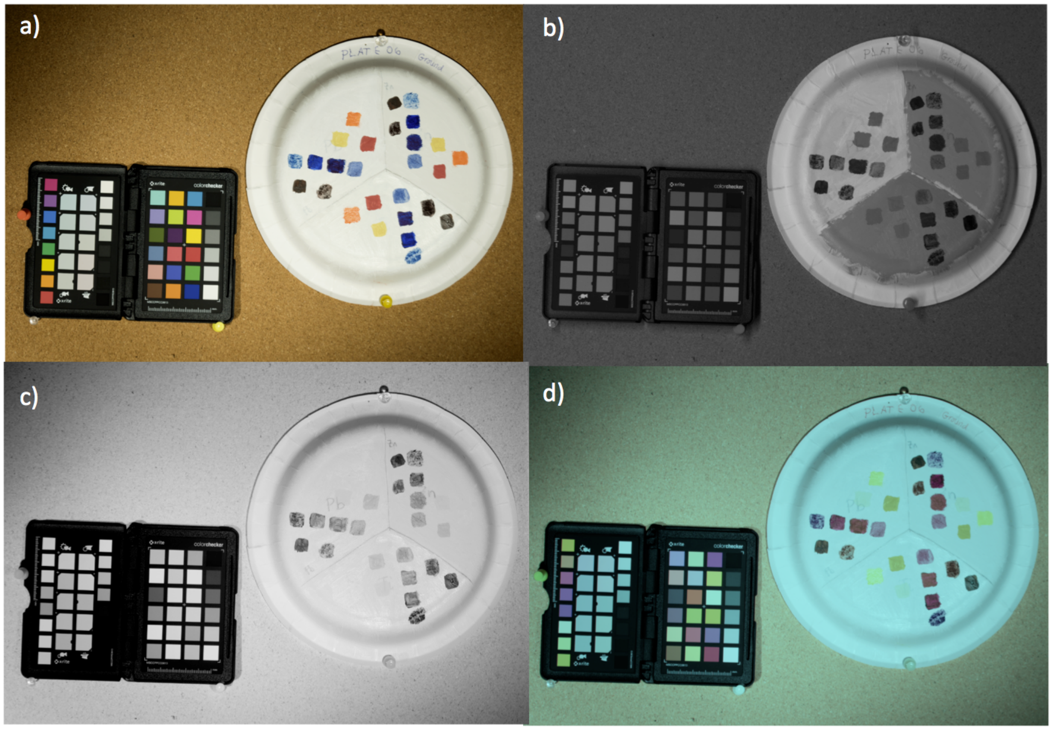

Figure 6.10. TP of Plate 6: Pigments layered on different white grounds. (Left third: Lead White; Right third: Zinc White; Bottom third: Titanium White.) a) VIS, b) UVR, c) IR d) IRFC.

of the setup and is to be accepted. For the layered weave this effect is obvious, but it is hardly noticeable in the case of the plate featuring different white grounds with colored swatches on top. Again, effort was made to duly wash the brushes and avoid contamination as much as possible.

The plates were imaged with a Nikon D810 DSLR camera with the in-built infrared filter removed, using a tripod setup with Solux Art lamps for illumination. Out of the images in the TP suite, UVR, IR (780nm cutoff), VIS, and IRFC were captured. The imaging studio and equipment available were not suitable for the UVF, IRF, IRR, or RAK modalities. The flowchart method described in [4] was modified accordingly to include only the imaging modalities able to be taken for this study.

XRF spectra were acquired with the same Bruker Tracer III-SD portable instrument. Spectra were acquired manually with a collection time of 60 seconds at 40 keV, 14uA; except in the case of Plate 5 (the weave layers) where the WAVEcam robot was used to position the instrument during collection.

6.2.2 Methodology

It was looked at how to process these datasets in attempt to answer some of the following questions. It was mentioned in the experimental setup that the exact mass ratio of the white and colored pigments could not be obtained for each swatch. There is some connection of the visible color produced through the tinting strength of the pigment to the quantity of material present, but let's suffice it to say that a calculation of pigment quantity would not be immediately useful, and thus it can be left out.

For the gradient plates, each swatch was analyzed using the TP flowchart to guide the pigment identification and see if the method fails to perform in any case. Results of the XRF analysis were then added as additional branches to the flowchart. The normalized areas under the XRF spectrum for the elements corresponding to the major components in each pigment were then plotted to show an estimated amount of pigment present. It was noted when a particular pigment could not be detected.

For the layered plates the post-processing procedure was aimed at determining if the flowchart resulted in a false conclusion in identifying the upper level pigment, and whether the XRF analysis could detect the lower pigment.

6.2.3 Preliminary Results

Qualitative observations can be detailed following the experiment. The gradient samples showed that lightening a pure pigment can very easily cause any TP metrics (ie. grayscale value for light vs. dark) for automated use of the flowchart to fail. For the most part XRF does not respond much better. Identifying the pigment from the spectrum alone becomes instantly more complicated when one or more of the peaks suddenly belongs to the white pigment instead. In all samples, by the second mixed swatch the colored pigment was already undetectable (allowing for a conservative noise threshold). This is due to the tinting power of the pigment requiring that not very much actual material be present to form the color we see, therefore there is less material to detect and we lose that ability easily. In a painting scenario, there should be enough areas with saturated colors to sufficiently define the palette of colors used.

In the layered scenario, the issue of transparency of certain pigments in certain regions of the spectrum (eg. they neither absorb nor reflect the incoming light) became apparent. The bottom layers would in this case be exposed. However, this happened rarely, and most upper pigments responded normally to the TP analysis. XRF was able to detect the underlying pigment in all cases, but this also did not obscure the reading of the top pigment to a trained specialist given the prior TP and visible information. The appearance of peaks from the bottom pigment in the XRF spectrum could easily disrupt an automated computer selection attempting to use the flowchart.

For colored pigments on top of different white grounds no major issues were observed. Most notable, was that in the UVR both Zinc and Titanium are absorbent and similarly responding pigments could be missed, though they are recovered in the visible and IRFC images. The main issue with XRF would be that the counts for the pigment can be diminished by the detection of the ground layer, but a proper subtraction should solve this. In the case of titanium the peaks could be mistaken for barium. This is one of the toughest mixtures to discern with XRF.

The plates experiment was a first look into the performance of the diagnostic exam and the initial methodological and processing concerns. As automated processing systems continue to be developed more testing will be necessary.

The material in Chapter 6 may be presented for publication at a later date.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

Currently, strategically obtained microsamples are still the best way to most definitively determine the palette of pigments used by the artist. They are doubly informative because they are stratigraphic and so the layering structure of the way the artist built up the painting can be understood. They can also be easily put inside the SEM and be analyzed with EDX, capturing an XRF spectrum with a spot size small enough to focus on a particle/granule of pigment and to home in on a particular layer. This process is invasive and requires access to a SEM, so it cannot be carried out on a large number of paintings.

Chapter 2 covered analytical techniques that are commonly used on cultural artifacts to identify and characterize the materials and artist's palette. These are mostly highly specific analytical tools, giving only a small piece of the puzzle in terms of information, and in many cases requiring advanced setups or expertise. There are several cases in the literature where researchers have been fortunate enough to form strategic collaborations in order to carry out a "multi-technique" approach to analytical diagnostics, which resulted in an effective characterization of the palette of pigments [70]. However, this way would also not be feasible to implement on a large scale.

The diagnostic exam presented in this dissertation will enable data leading to the identification of the artist's palette of pigments to be collected on a large scale. The design criteria have made it practical and affordable, while being robust and repeatable; ultimately yielding data that lead to conclusions in a reliable way. This will undoubtedly contribute to the creation of new knowledge, which will benefit the fields of art history and conservation. The diagnostic exam is one step within a methodological approach that takes inspiration from the field of medicine to introduce preventative diagnostics into the conservation of cultural heritage artifacts. Formulating such an approach, which can be considered a specialization between several traditional fields, has required an interdisciplinary skill-set.

Applications of the diagnostic exam were demonstrated in a fieldwork setting (Chapter 4), and advanced tools were developed to augment the user experience during acquisition, data management, and processing (Chapter 5). In the field the exam proved to be lean and adaptable, able to be implemented on-the-go with limited time on-site and portable equipment. The results were influential to inform further studies, especially in the case of the Chiesa Matrice wall paintings (Section 4.3). A critical exploration of the software tools used to elaborate and distill the results was carried out and documented in Chapter 3. These reduced forms of data are then input into the flowchart, whose design has been adapted to maximize the synergies between TP and XRF to provide accurate results for pigment identification. The number of pigments unable to be positively identified with either method alone was cut in half by using the two techniques together along with an improved flowchart tool to arrive at pigment assignments.

In Chapter 6, two case studies have utilized strategically prepared samples to test and validate the capabilities of the diagnostic exam. The study of the Pratt Madonna showed that when one branch of the flowchart takes a wrong turn, in some cases the correct assignment can be recovered by other characterizing features (such as elemental content) that trump an ambiguous imaging value assignment.

The diagnostic methodology is positioned to allow for future advancements in technology and developments in user-oriented tools to contribute to its improvement. The first demonstrations of these are the ones presented in Chapter 5. Some suggestions stemming directly from the work of this dissertation are discussed in the next section. This dissertation has presented a philosophical and methodological approach on how the field of cultural heritage diagnostics can begin to inform preventative conservation of artworks by taking steps to make an efficient and more automated use of current and future technologies. The first edition of the design for a diagnostic exam for the non-invasive identification of pigments in painted artworks was comprehensively shown.

The goal of this research is to influence the way we approach preventative conservation by proposing a solution meant to address many of the cumbersome aspects of the field, which have perhaps hindered progress in the past. It is also to suggest a methodological approach that is more analogous to the practice of medicine, as was advocated by a long time practitioner in the field, Maurizio Seracini. The research presents a series of case studies, which demonstrate the advantages of both approach and procedural method for the outlined objectives.

7.2 Impact on the Field and Broader Impacts

Let's say we liken the non-invasive pigment identification methodology for paintings described in this dissertation to diagnostics employed in the typical doctor's office – the nurse taking height, weight, and blood pressure when the patient arrives, before he or she is seen by the doctor. The data is taken and saved in the patient's file, their clinical chart. What impact do these data have in maintaining the prosperous health of the patient? Viewing the patient history could alert the medical staff to any abrupt or worrisome changes when they occur, including potential risk factors for future health complications (as is the case with blood pressure). Where the analogy of the practice of general medicine for the maintenance of human health breaks down when applied to the field of art conservation is that, unlike humans, the artifacts themselves cannot complain or voice their symptoms.

How then should we begin to assess the risk factors associated to the deterioration of a work of art, given especially, that paintings are continuously aging, and typically have centuries old histories that are for the most part undocumented and comprise unknown environmental scenarios? It is suggested that a good place to start would be to comprehensively document the pictorial surface of the painting and begin to determine how it has been made and what materials have been used. A basic anatomy is required to understand and develop a proper conservation protocol and is imperative if any consolidation work must be carried out in the name of preservation. The diagnostic exam described in this dissertation is designed to be an accessible routine examination that can be applied to all paintings in a standardized way. This will enable visual and materials data to be captured, linked, and retained in the clinical chart of the artifact, and for many artifacts to be analyzed in precisely the same way so that the all of the results can be reliably compared with one another independently of the practitioner who has acquired them.

It is already well visible that the advent of 'big-data' and 'open-data' practices have made an impact to the field of medicine, and moreover the practice of maintaining personal health. More data helps biological systems and risk factors to be better understood, enabling better conclusions to be made for the best course of action in a given patient scenario. By analogy, we can expect a similar effect in the field of conservation of cultural heritage. Trends for risk factors would be more easily identified and recommendations for preservation would follow verifiable data that demonstrate their effectiveness. In order for this vision to take place, however, the conservation world needs to start with a basic exam applied widely in general practice. How can the patient know which specialist to be referred to without a complete diagnostic workup? How can 'symptoms' be documented and tracked over time? Can we agree that heritage artifacts destined to outlast even our own existence deserve the type of personalized medicine that takes full advantage of the capabilities of modern technology?

The realization of the full potential and broader impacts of the transition of the conservation field, drawing useful and relevant expertise from the medical practice, and thus reaping the rewards inherent, requires that a simplified routine diagnostic exam be implemented - akin to the height, weight, and blood pressure taken during every doctor's visit. Its a place to start, and altogether not a simple feat, but it signals a philosophical change in the theory of heritage preservation that is one small step towards the full realization of the ability of modern technology to help preserve more of our collections, not just the pieces famous enough to travel on exhibition or turn heads in the title of the latest scientific study. The diagnostic exam developed through this research provides a democratic approach to cultural heritage diagnostics, successfully forming a basic building block of the digital clinical chart for heritage artifacts.

7.3 Future Research

Future research should continue with a rigorous testing of the automated interpretation pipeline proposed in this dissertation. The test scenarios shown in Chapter 6 can be expanded upon and quantitative metrics will need to be experimentally determined before full automation can be achieved.

Additionally, the research collaborators who are developing the tools, technologies, and infrastructures that enable the exam to be carried out will continue their development and innovation. This includes the WAVEcam team and data processing and storage system. The WAVEcam will also be adapted to become a truly mobile instrumentation.

Ideally, a collaboration will be sought after to digitize a small collection using the diagnostic exam, in order to have the first real-world dataset to work with.

It is intended that the diagnostic exam contribute to art historical research on the use of pigments and the evolution of the artist's palette. This is a long-term future research goal.

7.3.1 A Path to Chemical Imaging?

This research most likely has shown that the amount of data collected, that is, the density of spectral and elemental information can likely be pared down, without a great loss in understanding from strictly a materials standpoint. By going after the palette as a finite target for information, it is possible to economize the documentation scope. However, this does not necessarily translate to a loss of specific information and capability to differentiate between features and material changes within the painting. Instead, an area of innovation could be how to mine an economized dataset for the maximum amount of information possible. This will likely be achieved through advances in signal processing, segmentation, statistical analysis, and computational fields. It is predicted that a signal processing approach be applied to replicate chemical imaging as it is being undertaken today, using a reduced but dual-technique dataset and making calculated estimations in the spatial domain.

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