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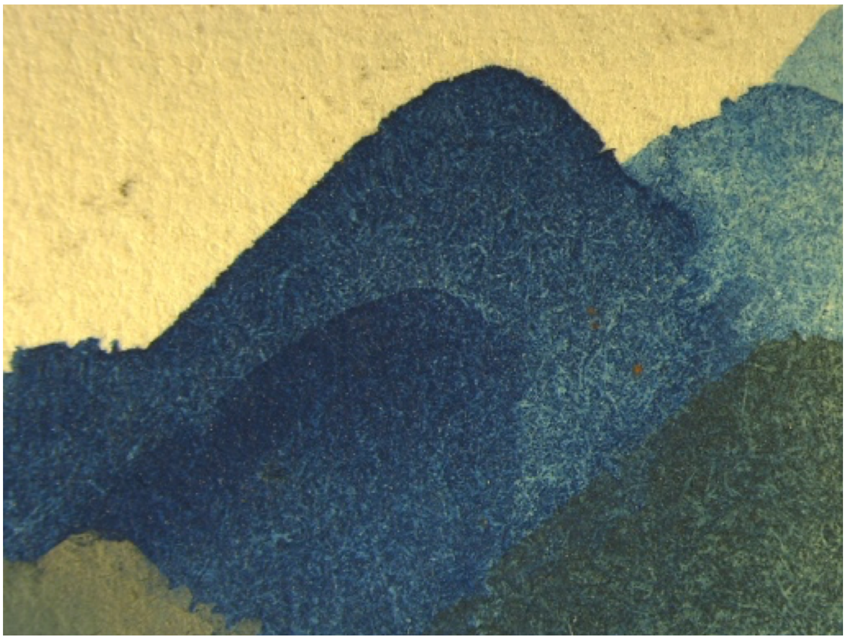
IDENTIFYING PIGMENTS

A Multi-Instrumental Study of Ivar Arosenius' Use of Pigments



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Identifying Pigments – A Multi-Instrumental Study of Ivar Arosenius' Use of Pigments

ABSTRACT

In this study, the pigments used by the Swedish artist Ivar Arosenius (1878-1909), in one of his sketch books (T 19/2001, Gothenburg Museum of Art), were examined and identified. The study used non-invasive and non-destructive analytical methods, and aims to determine what pigments Arosenius used and how well the analytical methods perform in examination of this particular object.

The basis for this study is the lack of knowledge about the use of materials by Arosenius. A three-year research project, called the Arosenius Project, is currently gathering information about the artist, aiming to digitize and make it more accessible for researchers and for the public. The project is based in Gothenburg and Stockholm and is funded by The Royal Swedish Academy of Letters, History and Antiquities and Riksbankens Jubileumsfond. The results of this study will contribute information to the project and to the general understanding of Arosenius' artistry.

Examination was conducted using optical microscopy, X-ray fluorescence (XRF), ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS), and multispectral imaging (MSI). The methods provided information about the color, chemical composition, and reflectance spectra of the pigments, as well as their properties in various spectral ranges. A probable identification is presented for 27 of 31 pigment samples in the sketch book. 15 different pigments have been identified, vermillion being the most frequently used. The study shows that the analytical methods are useful for pigment identification, but examination of objects of art is complex due to small areas of analysis, mixed and/or layered pigments, and to the consideration of the safety of the object.

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1. Introduction

1.1. Background

The Swedish artist Ivar Arosenius' (1878-1909) distinctive artistry and untimely death left a mark in Swedish art history, resulting in various portrayals and interpretations of the artist and his art. This vast and scattered body of information has led to a three-year research project called the Arosenius Project, which aims to gather information about the artist, digitize it, and make it more accessible for researchers and for the public. The participants of the project are the University of Gothenburg, Gothenburg University Library, Nationalmuseum, the Gothenburg Museum of Art (GKM), and The Swedish Literature Bank. By collecting all information known about Arosenius, as well as creating opportunities for acquiring new information through research, the project aims to create a comprehensive and historically informed image of Ivar Arosenius' life and artistry. One of the goals of the project is also to investigate how digital tools in museums can enhance or alter the visitors' experiences, as with virtual exhibitions. The digitization of Arosenius' art is a starting point for that investigation (Aroseniusarktivet 2016).

Ivar Arosenius was born on October 8, 1878, in Gothenburg, Sweden. He was brought up in a middle-class home where he learned to draw at a young age. Arosenius attended several prominent art schools during his lifetime, where he met and befriended many of the artists that would later rise to fame in Sweden. He married his wife Eva in 1906, and they became parents to a daughter, Lillan, who is the subject of many of Arosenius' most famous works of art. He died from a lifelong serious illness at the age of 30 on January 2, 1909 (Fredlund 2009). He received some recognition for his art during his lifetime, but it was not until after his death that he acquired national fame. Though an important figure in Swedish art history, little is known about what materials Arosenius used in his art, which is a crucial piece of information in order to fully understand his artistry, and can be of use for future conservation treatments of his work. This study aims to identify Arosenius' use of pigments in one of his sketch books.

The idea for this study emerged from a request by GKM to investigate the materials Arosenius used. It was also the author's desire to learn more about analytical methods, pigment identification, and pigment history. By using non-invasive and non-destructive analytical methods such as X-ray fluorescence (XRF), ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS), and multispectral imaging (MSI), pigments can be analyzed without sampling the object. In addition to pigment analysis, the digital documentation of the analyzed pages, resulting from the multispectral imaging, could eventually be used as a tool for conservation – a way to acquire as much information about an object as possible without having to subject it to sampling, destructive analysis, or unnecessary handling. As well as providing information about a prominent Swedish artist's use of pigments, this study is an example of how conservation science can contribute to art historical and conservation research.

1.2. Purpose, Aim, and Question Formulations

The purpose of the study is to contribute information to the Arosenius Project but also to the general understanding of Arosenius' artistry and use of materials. The results from this study could be of use for further research in conservation and art history. Although only a small part of Arosenius' artistry was examined, it can provide valuable information about his use of pigments and can be seen as a pilot study for how to conduct similar multi-instrumental experimentation on other works of art by Arosenius.

The aim of this study is to identify what pigments Ivar Arosenius used in one of his sketch books provided by GKM, by using non-invasive and non-destructive analytical methods. It is also to evaluate the analytical methods for their usefulness in this kind of examination, where the areas of analysis can be quite small and the pigments can be of low concentration or mixed with other pigments. The evaluation will be an indication of whether the identification process can be applied to other works of art. The question formulations in this study are:

- What pigments did Ivar Arosenius use in one of his sketch books (inventory number T 19/2001, Gothenburg Museum of Art)?
- How well do the chosen analytical methods perform in pigment identification for this object?

1.3. Methods and Materials

In order to answer the question formulations, literature about the analytical methods and pigment knowledge was studied. This step was crucial to the general understanding of the analytical methods and how they can be applied. Thereafter the experimental part of the study was conducted, first with optical microscopy, and then with the chosen analytical methods, which are energy dispersive portable X-ray fluorescence (XRF), ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS), and multispectral imaging (MSI). The data obtained from the analyses was examined and analyzed, and then interpreted with the pigment literature as a basis for interpretation. A list of paints purchased by Arosenius in Germany is also used as an indication of what pigments could be present. The results for all sketch book pages will be displayed in a table and the detailed process of interpretation is presented on one of the sketch book pages. Lastly, the results are discussed and the usefulness of the analytical methods evaluated.

1.4. Previous Research

There is no known research of pigment identification of works by Ivar Arosenius. There is, however, a great deal of research regarding pigment identification with the analytical methods chosen for this study, which was of help in conducting this study.

XRF is a widely used method for investigation in art conservation, pigment identification being one of its applications. Many articles have been written on the subject, several of them with the same goal as this study – to identify pigments using non-invasive and non-destructive methods. One such article used in this study is “Noninvasive and Nondestructive NMR, Raman and XRF Analysis of a Blaeu Coloured Map from the Seventeenth Century” (Castro et al. 2008). The anthology *Handheld XRF for Art and Archaeology* (Shugar & Mass 2012) acts as a guide for XRF knowledge, setup, and analysis. The publication is beneficial to anyone working with XRF spectrometers, but especially for those with minimal training in the field. One of the aims of the book is to provide operators of XRF spectrometers with the tools needed to obtain reliable results. The articles “X-ray analysis of Objects of Art and Archaeology” (Mantler & Shreiner 2001) and “Analysis of Art Objects and Other Delicate Samples: is XRF Really Non-Destructive?” (Mantler & Klikovits 2004) also provide information for the evaluation of XRF as an analytical method.

The scientific articles “Fibre Optic Reflectance Spectroscopy as a Non-invasive Tool for Investigating Plastics Degradation in Contemporary Art Collections: A Methodological Study on an Expanded Polystyrene Artwork” (Cucci et al. 2013), “Optical Measurements of Paintings and the Creation of an Artwork Database for Authenticity” (Hwang et al. 2017), and “Fiber Optics Reflectance Spectroscopy: A Unique Tool for the Investigation of Japanese Paintings” (Leona & Winter 2001) are used in obtaining information about UV-VIS FORS. These studies are conducted on materials other than paper, but as the information acquired relates to the instrumentation and application of UV-VIS FORS as an analytical method, they were still relevant for this study.

MSI is described in the scientific articles “Multispectral and Hyperspectral Imaging Technologies in Conservation: Current Research and Potential Applications” (Fischer & Kakoulli 2006) and “Advances in Multispectral and Hyperspectral Imaging for Archaeology and Art Conservation” (Liang 2012). The articles present the history of the method as well as its various applications. Detailed information on how to use the method and how to interpret the results, is described in "Identification of Pigments by Multispectral Imaging; a Flowchart Method", by Antonino Cosentino (2014b). Additional information about the analytical methods used in this thesis and how to conduct analytical experiments in general is provided by *Modern Analytical Methods in Art and Archaeology* (Ciliberto & Spoto 2000).

For pigment history and identification there are many helpful websites which present various pigments with their chemical compositions, dates of use, and reference spectra. In this study, the website *ColourLex* (Lipscher 2015) and the series *Artists' Pigments: A Handbook of Their History and Characteristics*, Volume 1-3 (Feller 1986; Fitzhugh 1997; Roy 1993), published by the National Gallery of Art, have been used for an overview of pigments. The *Artists' Pigments* handbooks offer a detailed history of many historical pigments, as well as their chemical compositions, and how to indentify them.

1.5. Restrictions

This study focuses on the pigment identification of one sketch book, T 19/2001. There are many other areas of interest in Arosenius' sketch books, such as paper and binder identification, but as time and resources were limited, analysis of these areas was not possible. The work with the sketch book was also restricted, as it is owned by GKM and cannot be removed from the premises due to safety and insurance policies. Three days were designated for analysis at GKM, and all analytical instrumentation from the University of Gothenburg was moved to the museum during this time. All analysis for this and two other students' studies was conducted in this time slot, which entailed a rather restricted time schedule for each analysis method. Three of the 12 sketch books in the Arosenius collection at GKM have various areas of paint, but due to the restricted time, only one was examined. The sketch book with the most colored areas was chosen for analysis to obtain the most information possible. The book contains areas of paint as well as pencil drawings, but only the paint was analyzed.

When conducting studies on pigment identification, literature suggests that a reference collection of known pigments should be used. Analysis of the known pigments should be conducted with the same instrumentation used for the experimental analysis. The data from both the known and unknown pigments can then be compared (Bacci 1995). However, due to budgetary and time restrictions, a reference collection was not used. Therefore, it is important to note that the results of this study are indications.

1.6. Ethical Considerations

The discussion of ethics is always important to consider in practical conservation. The potential risks of damage to the object are minimized by choosing non-invasive and non-destructive analytical methods, but there are always risks when working with cultural heritage objects. The most obvious risk is related to human error when handling the object. The object in this study is a bound material, which poses an elevated risk as the turning of the pages can strain the bindings. Precautions when operating the analytical instruments were taken by conducting the analyses with supervision by the study's mentor, Jacob Thomas.

The sketch book used in this study has several values – cultural, economic, and informational. Cultural and economic values are based on the legacy of Ivar Arosenius as a well-known artist who has a prominent place in Swedish art history. The informational values are described by Jonathan Ashley-Smith as "those that arise from hidden or exposed information that can be gleaned from an object or its associated documentation" (Ashley-Smith 1999). One could argue that the sketch book contains a large amount of hidden information that has yet to be exposed, such as choice of paper, binder, and pigments. This thesis can thus be of great importance for the informational value.

When working with museum objects one has a great responsibility both towards the museum and the object itself. In this study, no practical conservation takes place, but there are many ethical considerations when conducting analysis. According to Chris Caple (2000), analysis can be expensive, requires a lot of time, and it also poses risks for the object; thus, there should always be good justification for analysis. It is also important to choose analytical methods that are most likely to yield reliable results. The conservator should not only be able to operate the instruments but also to interpret the results, which can be difficult and time consuming. It is equally important to consider the state of the object and the justification of performing analyses on the object (Caple 2000). This study is not only justified by the request to examine the object, but also by the information that can be obtained. The results will increase the informational value of the sketch book and will be of use for the Arosenius Project, as well as the general legacy of Ivar Arosenius, which further justifies performing analytical examination.

1.7. The Need for Conservation Science in Conservation Practice

Conservation science is the use of science for conservation purposes, such as researching and evaluating various materials and treatments used in conservation practice. The term 'conservation science' was coined in the 1980s and has since become an important part of the conservation field (Townsend 2006). Examination of cultural objects is complex because of the objects themselves – they cannot be replaced and sampling is often not possible. The viewpoint of the conservator must always be with the object's wellbeing in mind. Sometimes examination must be conducted using advanced analytical methods, creating a need for analytical scientists and conservators to join forces. By identifying materials and processes, the understanding of objects of cultural heritage deepens (Adriaens 2005).

In *Contemporary Theory of Conservation* (2005), Salvador Muñoz Viñas points out that there not only exists conservation science, but also scientific conservation. He states that "conservation science is a branch of science which is practiced by scientists, while scientific conservation is a branch of conservation which is practiced by conservators" (Muñoz Viñas 2005). Per Muñoz Viñas' definition, this study would then be a product of scientific conservation, since the author belongs to the branch of conservation. However, the aim of the study was not directly linked to any specific conservation treatment and, in that aspect, is more scientific. On the other hand, the work is conducted on a museum object and the information from this study could be of use for future conservation treatments. It is not a simple matter to distinguish conservation science from scientific conservation and this study is a combination of both.

There are many advantages of pigment identification, such as obtaining knowledge about the chemical properties of a material. It is also a way of clarifying provenance, since many artists historically have mixed their pigments in characteristic ways, which could be used for authorship authentication. Pigment identification is also important for conservation purposes, since the chemical properties of pigments may affect how conservation treatments should be selected for specific objects. Identifying pigments is therefore useful in several fields – science, art history, and conservation (Stubbs 2013).

1.8. Terms and Definitions

Two terms that are frequently used in this thesis are "non-invasive" and "non-destructive". The terms can be confusing and are often used interchangeably. This study uses the terms according to Adriaens (2005) definition:

- Non-invasive: does not require sampling and will leave the object in the same state before and after analysis.
- Non-destructive: the sample or object can be analyzed repeated times but may require sampling to do so.

2. Analysis Methods and Study Material

The following chapter is divided in two parts. The first presents the analytical methods: optical microscopy, X-ray fluorescence, ultraviolet-visible fiber optic reflectance spectroscopy, and multispectral imaging. The second part presents the study material: a sketch book by Ivar Arosenius and a list of paints purchased by the artist in Germany.

2.1. Analysis Methods

2.1.1. Optical Microscopy

Visual observations with microscopy can provide basic information about pigments. Color, grain shape and size, as well as opacity are some of the properties that can be investigated with a microscope, but literature recommends sampling of the pigments so that they can be examined on glass slides in a polarized light microscope (Nyrén 1996). Because this study aimed to be both non-invasive and non-destructive, sampling was not an option. Microscopy therefore served as an examination of color and layering of pigments. It is recommended in most studies that basic information about the pigments is known before conducting the analytical investigation. This information greatly facilitates the analysis, since it will be easier to know what to look for in further examination (McGlinchey 2012).

2.1.2. X-ray Fluorescence

Energy dispersive X-ray fluorescence spectroscopy (XRF) is an analytical method that provides chemical elemental information about inorganic elements (Mantler & Schreiner 2001). It is a widely used method for art analysis and has become even more common with the emergence of handheld and portable XRF, which allows for *in situ* analysis. There are many advantages in using this method, such as the relatively low cost of instrumentation, easy usability, and the fact that it is possible to conduct non-destructive and non-invasive analysis (Shugar & Mass 2012). While XRF can be used as a sole investigative method, it is often used in combination with other methods of analysis. The complementary method is often one that can provide molecular information, such as Raman spectroscopy, since XRF can only provide elemental information (Castro et al. 2008).

The process with XRF begins with a photon that is emitted from the X-ray source (Figure 1). The photon interacts with atoms in the analyzed material. The primary photon usually causes an electron to jump out of the inner shell, the K shell, which in turn creates a vacancy. An electron from one of the outer shells will eventually fill that vacancy, as the inner shell, with its close proximity to the nucleus, is the most energetically stable place for an electron. Until the vacancy is filled, the atom is unstable. When an electron drops from an outer shell to

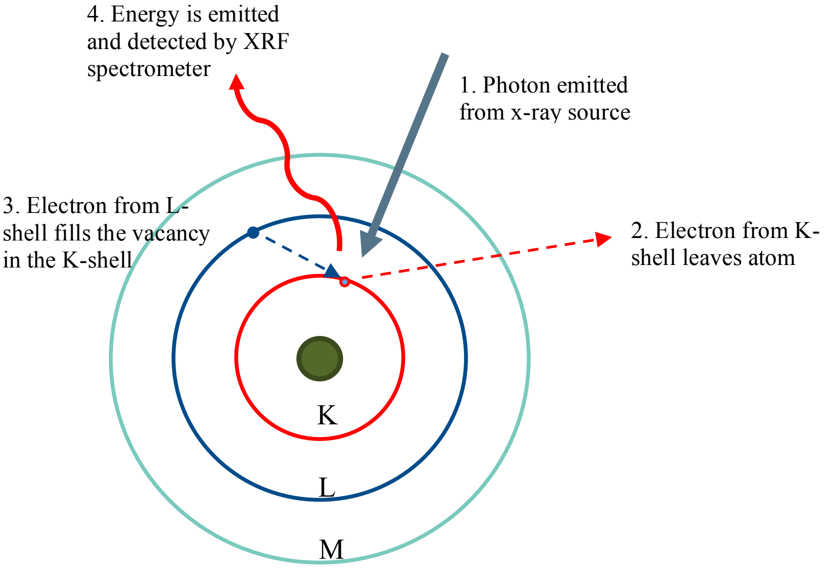

Figure 1. Illustration of X-ray penetrating an atom.

an inner shell, which has a lower energy level, it emits energy as an X-ray photon. The amount of energy released depends on the number of protons in the nucleus and from which shell the electron drops. The XRF-spectrometer detects the specific fluorescent energy and can consequently identify the element (Drake 2014).

The many positive aspects of analysis with a handheld XRF does not mean that it is simple. Interpreting data from XRF analysis requires knowledge about the physics of X-ray fluorescence. Art objects often consist of materials with a complex, heterogeneous nature and it is common that they are comprised of more than one material. These factors can complicate both analysis and interpretation (Shugar & Mass 2012). The area of examination of handheld spectrometers is 15 to 20 mm^2 in size, which is quite large when small areas of paint are examined. Handheld spectrometers are not as stable as the non-portable, which means that correct results are not always guaranteed. The nature of the analyzed material will also affect the level of difficulty in conducting and interpreting the analysis. Paper, for example, is a layered material and X-rays can penetrate several layers at once. This complicates the analysis since it can be unclear from which layer the data is collected (McGlinchey 2012).

It is also important to consider that false negatives and false positives can be produced in XRF analyses. A false negative may occur when elements are not shown in the XRF data, even though they are there. This can be caused when several elements have overlapping emission lines. False positives show elements or peaks in the XRF spectra that are not present in the sample or analyzed area. These peaks are called sum peaks and can be confusing to the interpretation of the data. False negatives and false positives may occur when analyzing mixed pigments, since there is more than one material present (McGlinchey 2012). XRF is considered a non-invasive and non-destructive method of analysis, but there have been studies suggesting that long measurement times can cause radiation damage to organic materials. However, with portable energy dispersive XRF, the measurement times are short enough for this not to be a problem (Mantler & Klikovits 2004).

2.1.3. Ultraviolet-Visible Fiber Optic Reflectance Spectroscopy

Reflectance spectroscopy has been used as an analytical characterization method since the 1930s. In recent decades, progress has been made in fiber optics technology which has increased the use of reflectance spectroscopy as an analytical method. Ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS) is a method that measures the optical characteristics of an object, where portable spectrophotometers with optical fiber probes record the reflectance spectra over the surface of an object (Cucci et al. 2013). This method operates mainly in the visible (VIS) spectral region and part of the ultraviolet (UV) region. These regions are part of the electromagnetic spectrum, which is the term for all radiation. The electromagnetic spectrum is divided by the various regions' characteristic wavelengths, measured with the unit nanometers (nm). The visible spectrum is the part of the electromagnetic spectrum that is visible to the human eye and lies between 380 and 780 nm, and the ultraviolet is approximately between 10 and 400 nm (Berns 2000, p. 3).

When an object is subjected to light, some of the light is reflected by the surface and some is absorbed into the material. Light can even pass through the material, if the material is transparent enough. The amount of energy reflected, absorbed, and/or transmitted is determined by the properties of the material (Bacci 2000). In this method, light passes through one of the two fiber optic probes at an

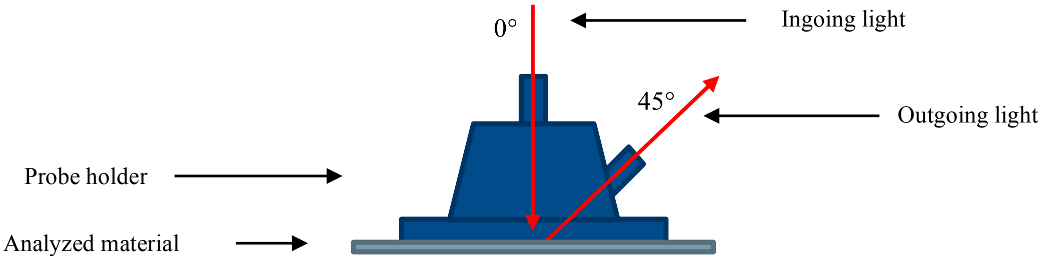

Figure 2. Light directed at the analyzed material at 0°. Light reflected from the material at 45°.

angle of 0° until it reaches the object. It is reflected from the surface at an angle of 45° and redirected back to the spectrometer through the other probe (Hwang et al. 2017), see Figure 2. Pigments can be identified by their characteristic reflectance or absorption peaks, but the quality of the recorded spectra varies, depending on, for example, the purity of the pigments (Bacci 2000).

There are many advantages with UV-VIS FORS, such as the capability to conduct non-invasive analysis and the ability to identify pigments. Many other methods can be used, but with UV-VIS FORS it is possible to identify pigments that are mixed or thin layered, which can otherwise be difficult to analyze (Leona & Winter 2001). With FORS it is also possible to acquire information about both chemical composition and colorimetric analysis (Cucci et al. 2013).

2.1.4. Multispectral Imaging

Multispectral imaging (MSI) has been used as an analytical tool in art conservation since the 1990s. It is a method where spectral and spatial information is gathered by collecting images at different ranges of the electromagnetic spectrum. It is a quick, non-invasive method and functions in many areas of wavelength (Liang 2012). As MSI operates in such a broad range of spectral bands, it has the advantage of functioning as several analytical methods combined. With MSI, it is possible to reveal underdrawings, identify pigments, map pigment distribution, identify binding media, and is also used for digital documentation (Fischer & Kakoulli 2006).

The spectral bands used in this study are: UV, VIS, and infrared, IR (780-1100 nm). The VIS-region provides the most basic information about the analyzed area – the color. Results from the UV region pertain only to the surface layer of a paint, since ultraviolet light cannot interact with what is underneath the surface layer. In UV reflected (UVR) a pigment can either be bright or dark. In UV fluorescence (UVF) pigments can be identified by their characteristic fluorescent color or lack of fluorescence. In the IR region, a pigment can be classified as bright or dark, depending on its transparency, reflectance, and/or absorbance. The layer underneath the pigment, whether it is an additional pigment layer or paper, largely affects the results of the IR image (Cosentino 2014b).

MSI is a useful tool in pigment identification if the pigments are pure and single layered, but becomes problematic when the pigments are mixed and/or consist of several layers. It is recommended that at least one other method for identification be used if the results are to be reliable (Cosentino 2014b).

2.2. Study Material

2.2.1. Sketch book

For this study, a sketch book by Ivar Arosenius was examined. The sketch book, from 1908, is in the Arosenius collection at GKM and has the inventory number T 19/2001. The book measures 24.0 x 16.3 cm. The sketch book has six pages with 31 areas of paint. The areas vary in color, size and thickness, and are often overlapping, see Figure 3.

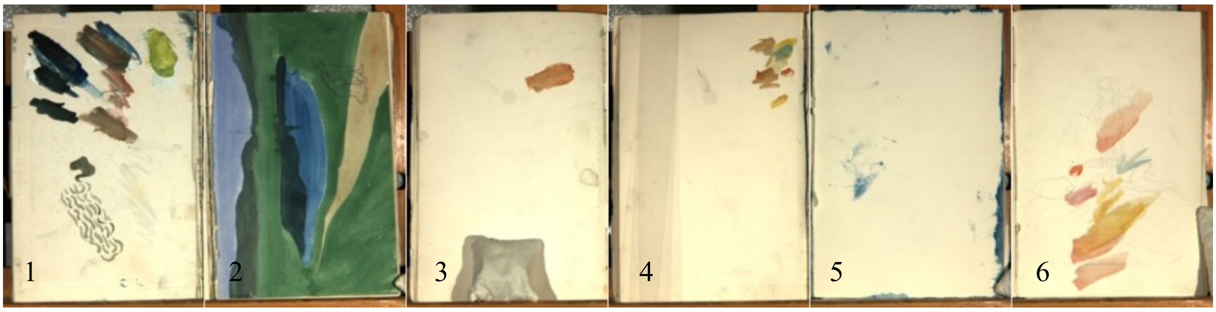

Figure 3. Pictures of the pages (1-6) of sketch book T 19/2001 which are analyzed in this study.

2.2.2. List of paints

While there is very little information about Arosenius' use of pigments, he did take a liking to high-quality pigments, such as those of the brand Winsor & Newton. He used many different medias during his lifetime, but eventually watercolor became his main medium (Fredlund 2009). In a document provided by GKM, a list of paints purchased by Arosenius in Germany on July 23, 1907, are presented, see Table 1. The list is marked with the company's name 'L. Boessenroth, Kunstmaler' and lists the quantity of the tubes as well as the price (see Appendix 1). In the document, the word 'tempera' appears several times, so it is probable that the tubes of paint were of the media tempera. While the binding media is not analyzed or discussed in this essay, it is worth mentioning that the media in the sketch book is believed, by the author, to be gouache and/or watercolor. The list is therefore only an indication as to what pigments Arosenius might have preferred since the same pigments used in tempera can be used in gouache and watercolor as well.

Table 1. List of paints purchased by Arosenius in Germany 1907. English translations by the author.

German	English
Kremserweiss	Lead white
Cadmium hell	Cadmium bright
Terra Siena nat.	Sienna earth, natural
Terra Siena gebr.	Sienna earth, burnt
Zinnober echt	Vermillion, pure
Wurzelkrapp dunkel I	Madder lake, dark
Cobalt echt I	Cobalt pure
Ultramarin	Ultramarine
Cobaltgrün hell	Cobalt green bright
Elfenbenschwarz	Ivory black

It is worth noting that the second pigment on the list, cadmium bright, could be any cadmium-containing pigment, but as it is listed among other yellow pigments in the document, it is believed to be cadmium yellow. The pigment 'cobalt pure' could also be any cobalt-containing pigment, but as it is listed among the blue pigments in the document, it is believed to be cobalt blue.

3. Experimental

The optical microscopy and the analyses with XRF, UV-VIS FORS and MSI were carried out in the paper conservation studio at GKM. Supervision was provided by Jacob Thomas and Mariateresa Pullano, paper conservator at GKM.

3.1. Optical Microscopy

Optical microscopy was conducted with a Leica M80 stereo microscope (Figure 4), with a maximum magnification of 60x (Leica Microsystems 2017). Images at 7.5x and 60x were taken.

Figure 4. Microscopy setup: visual examination of the pigments in sketch book T 19/2001, with Leica M80 microscope.

3.2. XRF

The XRF-analyses were conducted with an Olympus Premium portable XRF spectrometer, in a Mining+ mode (Olympus 2015). An analysis was conducted for each sample area, as well as the corresponding paper for each page. One analysis consists of two exposures. The first exposure identifies heavy elements and the second identifies light elements. The settings of the exposures are listed in Table 2.

Table 2. XRF settings for exposure 1 and 2.

Settings	Exposure 1	Exposure 2
Voltage	40 kV (kilovolt)	10 kV
Filter	Thick aluminum filter	No filter
Current	21.1 µA	16 µA
LT (live time)	20 seconds	20 seconds

The spectrometer was held in place with a stand during analyses (Figure 5). A board of plexiglass was placed on the baseboard as to maximize the area where the sketch book was positioned. The sketch book was then positioned on the plexiglass, with the page to be analyzed lying face-up. The book itself was supported by sandbags to minimize the risk of straining the spine. A protective cover window of Melinex with a cut out rectangle of 2x2 cm was placed between the instrument and the page in order to solely expose the analysis area.

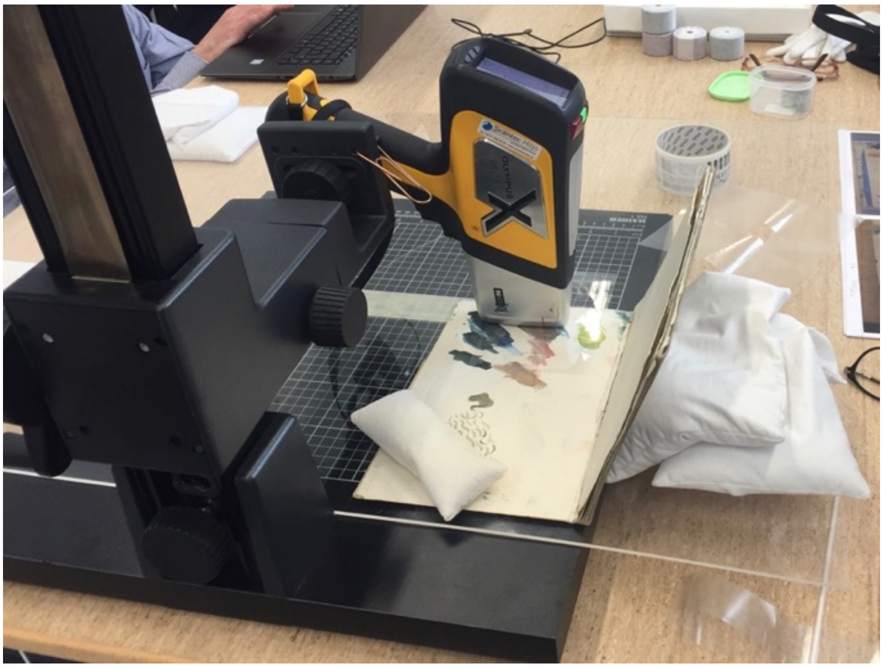

Figure 5. XRF analysis setup: analysis of inorganic elements of the pigment areas in sketch book T 19/2001 with XRF spectrometer.

Because of the penetrating nature of X-rays, there is a risk of interfering fluorescence from underlying pages when working with bound material. To minimize this risk, a material, with a low atomic number undetectable by XRF, can be put between the pages to block the interfering fluorescence from the pages below (Trentelman et al. 2012). In this study, a piece of plexiglass, measuring 28x20 cm, wrapped in non-woven polyester, was put between the pages. The plexiglass was not used for page 1 where the paper is attached to the cover.

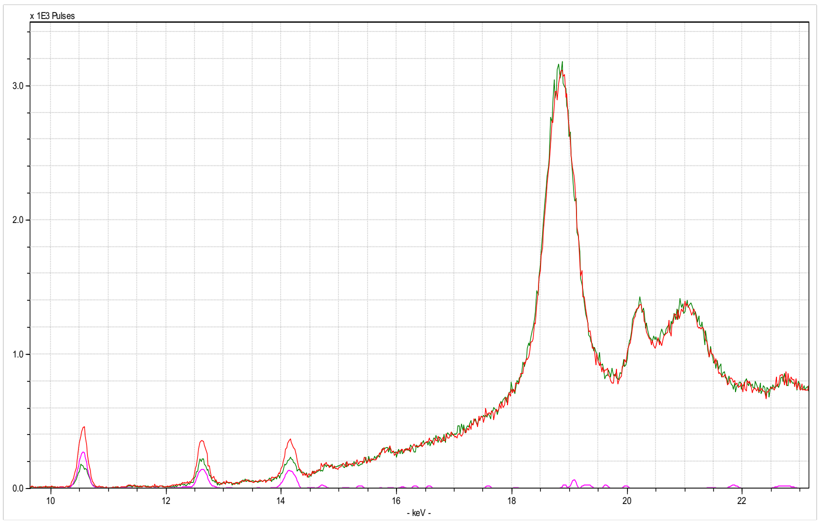

Figure 6. The original sample spectrum (red), the paper spectrum (green), and the subtracted spectrum (pink) of sample 2A.

The recorded spectra were analyzed using Bruker Artax-software (provided by Informant 1). The XRF-spectrometer does not discriminate between the paper and the painted surface, so the data contains information about both. Therefore, the paper-spectra was subtracted from each of the sample-spectra, creating a new spectrum with only the subtracted paint layer. Certain elements, which can be found in paper, such as calcium or iron, can also be found in pigments. If the data from paper was not subtracted, it could lead to faulty interpretations. This is illustrated in Figure 6, where the original sample spectrum (red line), paper spectrum (green line), subtracted spectrum (pink line) are presented. The spectral peaks between 18 and 22 keV (kiloelectronvolt) are not included in the subtracted spectrum, and are thus not components of the pigments, but the paper. Subtracting the paper-spectra is thus beneficial to the level of accuracy of the interpretation.

3.3. UV-VIS FORS

For the collection of the reflectance spectra, a portable Qmini Wide spectrometer, manufacturer RGB Photonics, was used (RGB Photonics 2016). The spectrometer has a working range of 220 – 1050 nm with a resolution of 1.2 nm. Exposure time for each analysis was 107.75 ms (milliseconds), averaging 20. A 4-LED light engine was used, see specifics listed in Table 3. A 2 meter, High OH fiber optic, cable with a cord diameter of 400 µm (micrometer) and 0.5 NA (numeric aperture), and a 0° - 45° fiber probe was used, (Figure 2).

Table 3. Specifics of 4-LED light engine (Mightex Systems Full spectrum light source) used for UV-VIS FORS analysis.

Channel	Maximum capacity	Used at	Properties
C1	1000 mA (milliamps)	250 mA	Warm white LED
C2	1000 mA	250 mA	740 nm center λ max
C3	500 mA	250 mA	420 nm center λ max
C4	500 mA	0 mA	385 nm center λ max

The sketch book was positioned on a table with protective non-woven polyester underneath. The probe was positioned directly on top of the sample, see Figure 7. A sheet was used to block any possible interfering reflectance from underlying pages. The sheet was made of cotton paper wrapped in aluminum foil, covered in protective Melinex.

The recorded spectra were examined in Waves RGB Photonics software (RGB Photonics 2017). Reference spectra with pure pigments in gum arabic from the FORS Spectral Database of Historical Pigments in Different Binders were downloaded and compared to the collected reflectance spectra. The spectral database consists of spectra of 56 historical pigments (Cosentino 2014a). The lambda (λ) max, which are the spectral peaks, and the overall shape of the spectra were examined and compared to the reference spectra. When the reflectance spectra were inconclusive or if there were specific regions of interest to examine, the first derivative was applied. The first derivative spectrum is when a derivative transformation is applied to the original data, which is useful for easier discrimination (ASD Inc. 2017).

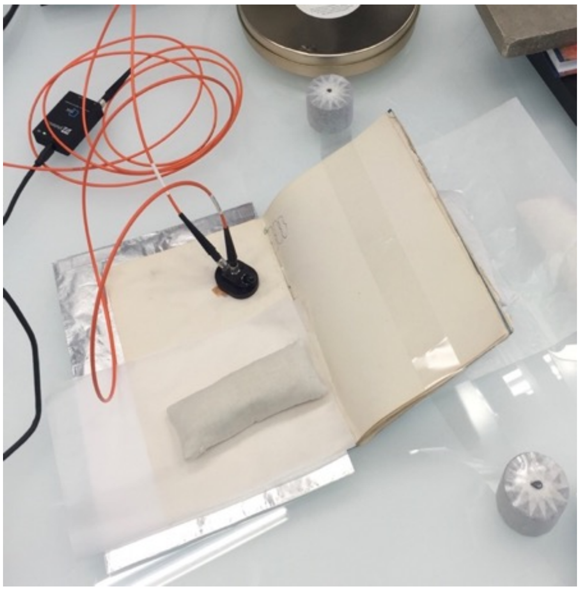

Figure 7. UV-VIS FORS setup: collection of reflectance spectra of the pigment areas.

3.4. MSI

MSI was conducted in a semi-dark room with an Artist Camera from Art Innovation. The camera has 5 MP (megapixels) Panchromatic CMOS sensor without IR filter, with a Schneider Kreuznach Xenoplan 1.4/23 CCTV-lens (400-1000 nm). It has an internal filter wheel with 7 positions (Art

Innovation 2015). The camera was calibrated on a 17% grey card. Images were collected in visible (VIS), red-green-blue composite image (RGB), infrared (IR), ultraviolet reflected (UVR), and ultraviolet fluorescence (UVF), see specifics in Table 4.

Table 4. Settings for MSI channels.

Channel	Aperture F stop	Filter
RGB	5.6	Red, green, blue filter with IR COF (cut off filter)
VIS	5.6	UV-IR COF
IR 2	2.8	BP (band pass) 900-1000 nm
UVR	2.8	Internal UV SP (short pass)
UVF	2.8	UV-IR COF with external 400 nm LP

The sketch book was positioned on an easel, see Figure 8. When necessary, sandbags were used to keep the book in place. Images were analyzed in ImageJ software (ImageJ 2017). Infrared false color (IRFC) images were created by splitting the RGB image into three channels - red, blue, and green - thereafter merging the IR image with the red and green channels. The IRFC images are used to better distinguish the pigments (Cosentino 2014b). Images in RGB, VIS, IR 2, IRFC, UVR, and UVF were put together in a montage where the areas of analysis can be compared in the different spectral regions. The areas of interest were analyzed according to Antonino Cosentino's flowchart method, where 56 historical pigments have been tested (Cosentino 2014b). An example of a flowchart for blue pigments is presented in Figure 9. The selection of pigments in the example flowchart is based on results presented later in the study (see Table 5).

Figure 8. MSI analysis setup: collecting images of the pigment areas in various spectral bands.

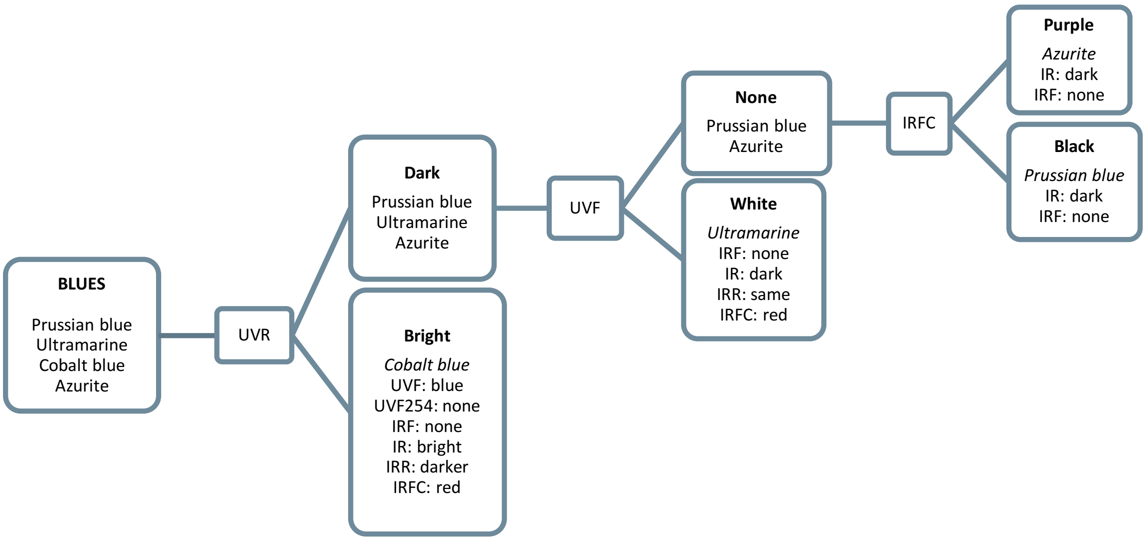

Figure 9. Example of a flowchart for the identification of blue pigments.

4. Results

In this chapter, all the results from the pigment identification are presented in a table. The table is divided into sections: the name of the sample, the visible color, observed layering, the results of the MSI (UVR, UVF, IR, IRFC), the elements found by XRF, and the peaks of the reflectance spectra presented in λ max, a probable identification (when possible), and analytical methods suggesting the probable identification (1 = MSI, 2 = XRF, 3 = UV-VIS). The elements in bold text are the main elements which correlate with the probable identification. A parenthesis around the method number indicates that an identification with the method is not as reliable as the other methods.

Table 5. Results of the pigment identification are presented in this table. The first three columns contain the samples' name, color, and layering. Thereafter the results from MSI, XRF, and UV-VIS FORS are presented. The last two columns show a probable identification and which of the analytical methods that support the identification.

ID	Color	Observed layering	MSI				XRF		UV-VIS FORS	Probable ID	Suggested by methods
			UVR	**UVF**	**IR**	**IRFC**	**40 kV**	**10 kV**	**λ max (nm)**		
1A	Blue	No	Dark	None	Dark/bright	Purple/Red	Pb, Zn	Pb, Cr	510	Ultramarine	1,(3)
1B	Green	Yes	Dark	None	Bright	Pink	Pb, Hg, **Cd**	Pb, Cd	550	Cadmium yellow + unidentified pigment	2,3
1C	Blue	Yes	Dark	None	Dark	Purple	Pb	Pb	460	Ultramarine	1,3
1D	Brown	Yes	Dark	None	Dark	Brown	Pb, **Hg**	Pb, Hg	610	Vermillion + unidentified pigment	2,3
1E	Red	Yes	Dark	None	Bright	Yellow	Pb, **Hg**	Pb, Hg	610	Vermillion	1,2,3
1F	Blue	Yes	Dark	None	Dark	Black	Pb, **Fe**	Pb, Fe	450	Prussian blue	1,2,3
1G	White	No	Bright	Orange	Bright	White	**Pb**, Hg	Pb	500	Lead white	2,3
1H	Green	No	Dark	None	Dark	Black/Purple	Pb, Zn, **Fe**	Pb, Fe	520	Green earth	(1),2,3
1I	Brown	Yes	Dark	None	Dark?	Brown	Pb, Hg	Pb	600	-	
1J	Green	No	Dark	None	Dark	Black/Purple	Pb, Hg, **Fe**, Zn	Pb, Hg, Fe	580	Green earth	1,2,3
2A	Blue	No	Bright	Blue	Bright	Red	Pb, **Co**, Fe, Cd, Sr	Co	500, 690	Cobalt blue	1,2,3
2B	Green	Yes	Dark	None	Dark	Red	Pb, Fe, Hg, **Cu,** Sr	Pb, Fe	530	Verdigris	1,2,(3)
2C	Green	No	Dark	None	Dark?	Pink	Pb, Hg, Fe, **Cd,** Sr	Pb	520	Cadmium green	(1),2,3

2D	Blue/Green	Yes	Dark	None	Dark	Purple	Pb, Fe, **Co**, **Cu,** Hg, Sr	Pb, Fe	500	Cobalt blue + verdigris	2
2E	Blue	Yes	Bright?	Blue	Dark	Purple	Pb, **Fe**, **Co**, Hg, Sr	Fe	470-480	Prussian blue / Cobalt blue	2,(3)
3A	Brown/Orange	No	Dark	None	Bright	Orange	Pb, **Fe**, Cr	Fe	600	Raw sienna	2,3
4A	Yellow	No	Dark	Orange	Bright	White/Orange	Pb, Hg, Cr, **Co**	Pb	550	Cobalt yellow	2,3
4B	Brown	No	Dark	None	Dark	Brown	Pb, **Fe**, Hg, Ca	Pb, Fe	600	Raw sienna	2,3
4C	Red	No	Dark	None/red	Bright	Yellow	Pb, **Hg**	Pb, Hg	610	Vermillion	1,2,3
4D	White/Yellow	No	Bright?	Orange?	Bright	White	Pb, Hg	Pb	530	-	
4E	Blue	Yes	Dark	None	Dark	Purple	Pb, Hg	Pb	530, 600	-	
4F	Yellow	No	Dark	Orange	Bright	White	Pb, Hg	Pb	540	Gamboge	3
4G	Brown	No	Dark	None	Bright	Brown	Pb, Hg, Cd, **Fe**	Pb, Fe, Cu	590	Raw sienna	2,3
5A	Blue	No	Dark	Blue	Dark	Purple	Pb, Cd, Fe, **Cu,** Zn	Pb, Fe	480	Azurite	2,3
6A	Red	No	Dark	None	Bright	Yellow	Pb, Hg	Pb, Hg, **Cd**	600	Cadmium red	1,2,3
6B	Red	Yes	Dark	None	Bright	Yellow	Pb, **Hg**	Pb, Hg	600	Vermillion	1,2,3
6C	Yellow	Yes	Dark	None	Bright	Yellow	Pb, Hg	Pb, Hg	550	Gamboge	1,3
6D	Pink/Purple	No	Dark	None	Bright	Yellow	Pb, Hg	Pb, Hg	550, 610	Ultramarine + vermillion + red lead	2,3
6E	Red	No	Dark	None	Bright	Yellow	Pb, **Hg**	Pb, Hg	600	Vermillion + red lead	1,2,3
6F	Red	No	Dark	None	Bright	Yellow	Pb, **Hg**, Cu	Pb, Hg	600	Vermillion + red lead	1,2,3
6G	Blue	No	Bright	Blue	Dark?	Purple/red	Pb, Hg	Pb, Hg	490	-	

5. Interpretation

In this chapter, the interpretation for Page 1 of sketch book T 19/2001, GKM, will be presented, as an example of how the interpretation process is conducted. The same process was applied to each page. Examples of microscopy images, MSI images, reflectance spectra, and XRF spectra will be presented to better explain the interpretation process.

5.1. Page 1 - An Explanation of the Interpretation Process

Before an interpretation can be conducted, it is important to separate the terms 'color' and 'colorant'. The colorant is the pigment or dye, and the color is the properties of the pigments and dyes. While there are certain characteristic properties of colorants, it is not possible to consequently assign a color to a colorant, since the variations are so vast. A specific color can be produced by many different colorants, and colorants can produce a large variety of colors. Pigment mixtures have been used for creating colors which could otherwise only come from pigments that might have been scarce or very expensive (Stubbs 2013). Because of the many variations of colors that pigments can produce, an accurate identification of unknown pigments calls for more than optical examination which, however, can work as a primary indication. The identification process therefore begins with a visual examination of the painted area in order to get a sense of color and determine if there are layers of different pigments. Documentation pictures and microscopy images can be of help in this step. The results of the MSI, UV-VIS FORS, and XRF are reviewed and analyzed. When a probable result has presented itself, the provenance of the probable pigment is established, which can help determine if the pigment was in use in 1908 when Arosenius produced the sketch book. The list of paints (see Table 1), the website *ColourLex*, and the *Artists' Pigments* handbooks are of help in this step.

Page 1 has ten areas of analysis (referred to as samples) and have been labelled 1A-1J see Figure 10. The areas of analysis for all pages can be found in Appendix 2. Microscopy images for all samples can

Figure 10. Page 1 of sketch book T 19/2001, sample 1A-1J.

be found in Appendix 3. MSI images for all pages can be found in Appendix 4. Reflectance spectra from UV-VIS FORS can be found in Appendix 5 and result reports from XRF can be found in Appendix 6.

After establishing a color for the sample, its layering is examined. Layers are not always easy to distinguish, but sometimes they are obvious, as in Figure 11, where a white layer can be seen underneath the green. Figure 11 can be compared to Figure 12, where there is no layering of different pigments. The distinguishing of layers is important because it affects the reliability of the results. As previously mentioned, MSI is very limited if the areas of pigment are layered or mixed. Therefore, the MSI results for layered areas are not as reliable as for those not layered. This is also the case for mixed pigments, but it is difficult to determine whether a pigment is mixed or not without examining the grains of the pigments, which was not possible in this study, as it would require sampling.

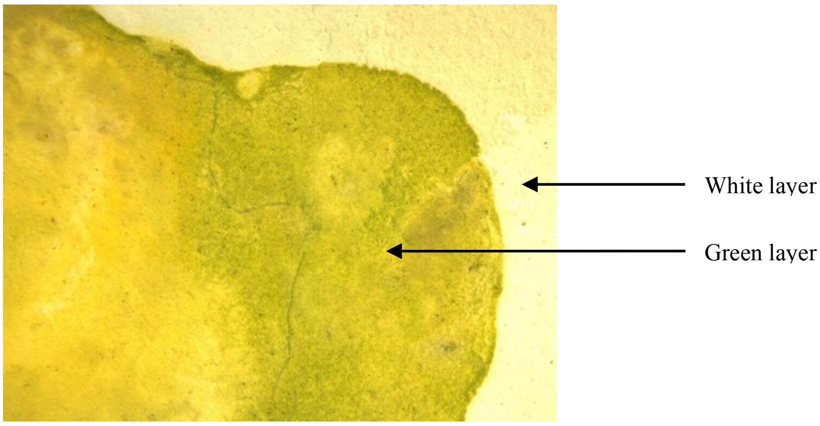

Figure 11. Microscopy image (magnification 7.5x) of sample 1B. Layers and possible mixes of pigments.

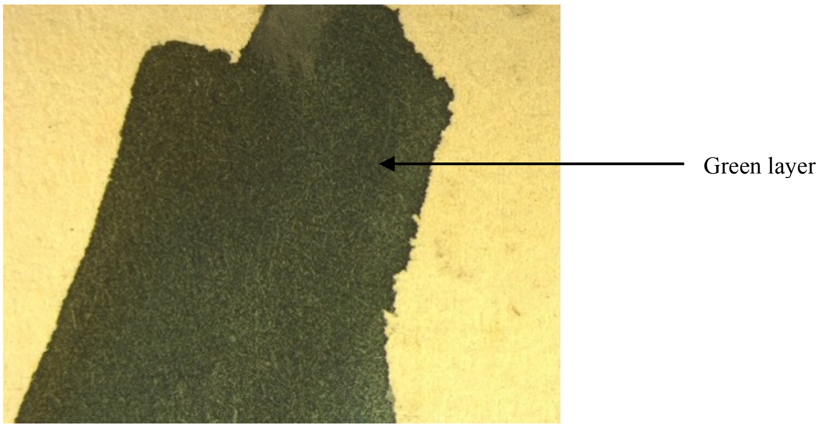

Figure 12. Microscopy image (magnification 7.5x) of sample 1H. No evident layers or mixes of multiple pigments.

The flowchart method is applicable for white, blue, green, yellow, and red pigments (Cosentino 2014b). Of the ten samples in page 1, two were excluded from the MSI interpretation since they are brown. It is also worth mentioning that the XRF analysis showed traces of lead in all samples. One explanation for this could be the use of lead white, which was the primary white pigment until the end of the 19th century, when it was replaced by zinc white which is less toxic (Lipscher 2015). Lead white has been used as a white pigment but also for lightening other pigments, and in various media such as oil, egg, and gum arabic, which is the binding media for watercolor (Roy 1993). In the list of paint purchased by Arosenius, lead white is included. He could have used the pigment for white areas but also as a filler in his paints.

5.1.1. Sample 1A

A is blue and appears unlayered but there are dark areas in the sample which could entail multiple pigments. The sample appears dark in UVR, does not emit fluorescence in UVF, and appears purple/red in IRFC (Figure 13). There are both dark and bright areas in IR, which could mean that there are several pigments present. Based on the flowchart method, if the IR is dark, it could be either azurite or ultramarine. Azurite is a mineral and contains copper (Roy 1993). The results from the XRF show that no copper is present in the sample, so azurite is an unlikely pigment. Ultramarine is made from the mineral lapis lazuli, and has been in use approximately since the 7th century. Artificial ultramarine was invented in 1828 and eventually replaced the very expensive natural ultramarine (Roy 1993). According to the flowchart, Maya blue, indigo, or phthalo blue are possible results if the IR is bright. Indigo is an organic pigment which has been used since antiquity and is still in use today, mainly in textile dyeing and watercolor. Maya blue has mostly been used in wall paintings and for ceramics in Central and South America (Roy 1993). Phthalo blue contains copper and is a synthetic pigment that was first invented in the 1930s (Lipscher 2015). Therefore, indigo or artificial ultramarine are the most likely pigments. They are, however, difficult to distinguish from another, in terms of their chemical compositions. Ultramarine contains sodium, which is undetectable with XRF, and sulphur and aluminum, which can be difficult to detect with XRF (Trentelman et al. 2012). The reflectance spectrum is inconclusive, but a slight peak in the 450-550 nm region could indicate ultramarine, which has a distinctive peak at about 460 nm. Ultramarine is on the list of paints that Arosenius bought in Germany, which increases the possibility of the sample being ultramarine. It is also possible that the sample is a mix of ultramarine and indigo, since there are both bright and dark areas in IR.

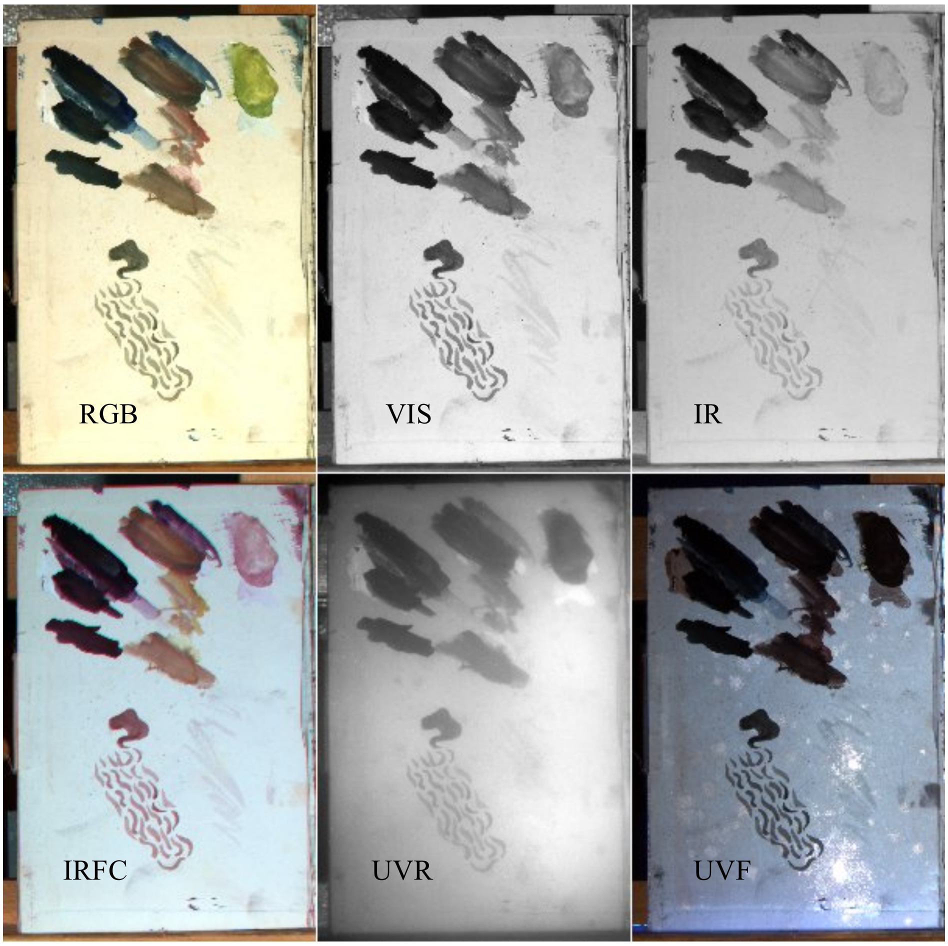

Figure 13. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 1.

5.1.2. Sample 1B

1B is green and appears layered. Consideration should always be taken when analyzing green colors, as it is possible that they are a mix of a blue and yellow pigment (Cosentino 2014b). The results of the XRF weigh more heavily than the results of the MSI when examining layered samples. According to the flowchart, the sample could be cadmium green, cobalt green, or chrome green. XRF shows that cadmium is present in the sample, which most likely means that the pigment is cadmium green. However, since the sample is green, it could also be cadmium yellow or cadmium blue, mixed with a blue or yellow pigment respectively. The reflectance spectrum is a better match with cadmium yellow than cadmium green, based on the distinctive peak at around 550 nm. Cadmium yellow is also listed amongst the paints purchased by Arosenius. The pigment was discovered in 1818 and has been widely used in various forms since the 1840s (Feller 1986). If the sample consists of cadmium yellow, a blue pigment should also be present. The data does not provide enough information to determine which blue pigment could be present, but indigo or ultramarine are the most probable since there is no copper, iron, or cobalt present.

5.1.3. Sample 1C

1C is blue and appears layered. It is dark in UVR and IR, emits no fluorescence, and is purple in IRFC, which indicates azurite. However, XRF shows no signs of copper. Copper is easily detected by XRF so if the data does not show copper there probably is none. The reflectance spectrum shows a peak at around 460 nm, which is a match with the reference spectrum for ultramarine (Figure 14). MSI could indicate ultramarine as a possible result as well, if the color in IRFC is red and not purple. Red and purple results in IRFC can often be confusing, and the color balance of the images can have a great impact on the results (Informant 1).

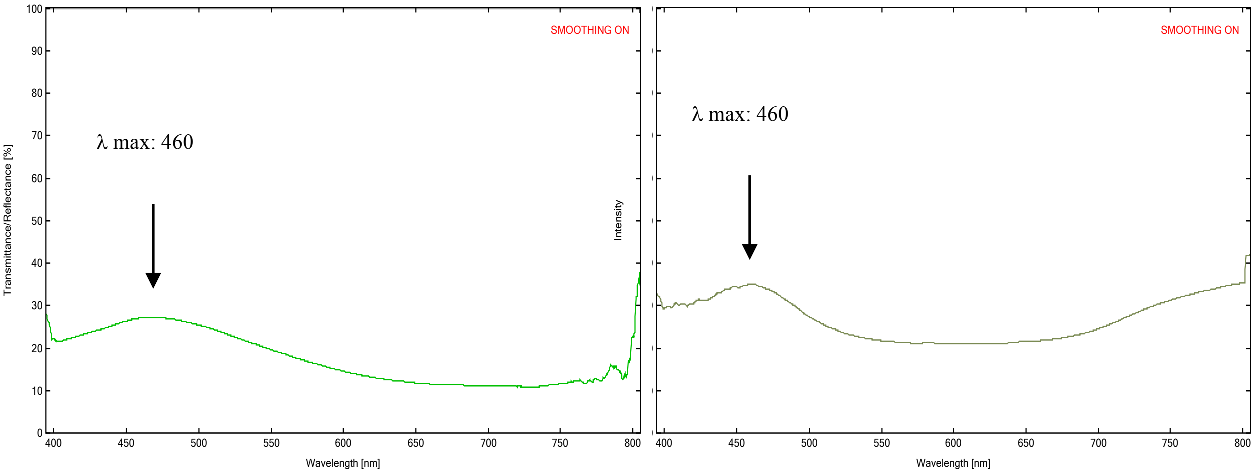

Figure 14. Left: UV-VIS FORS reflectance spectrum of sample 1C. Right: Reference spectrum of the pigment ultramarine in gum arabic.

5.1.4. Sample 1D and 1E

1D is brown, which is a color that is not included in the flowchart. It is, however, evidently layered and the brown color could be a result of a mixture of several colors, one being red. XRF shows traces of mercury in the sample, which could indicate that the red pigment is vermillion, a pigment that has been used since antiquity (Roy 1993). This is corroborated by the fact that the next sample, 1E, is red and most likely vermillion, due to the presence of mercury and the results of the MSI (UVR: dark, UVF: none, IR: bright, IRFC: yellow). The reflectance spectrum for 1E has a distinctive peak at around 610 nm, which correlates with the reflectance spectrum for vermillion in the database. 1D also has a peak at the same wavelength, although it is not as distinctive.

5.1.5. Sample 1F

1F is blue and appears layered. It is dark in UVR, does not emit fluorescence in UVF, is dark in IR, and black in IRFC, which according to the flowchart indicates the pigment Prussian blue. Prussian blue contains iron and is a synthetic pigment which was commonly used between the 1730s and 1970s (Fitzhugh 1997). The presence of iron in the sample is confirmed by XRF, increasing the reliability of the probable identification. The reflectance spectrum shows a peak at 450 nm, which corresponds with the reflectance spectrum for Prussian blue.

5.1.6. Sample 1G

1G is white and does not appear to be layered. It is bright in UVR, orange-brown in UVF, bright in IR and white in IRFC. It does not correlate with any of the pigments in the flowchart, with the possible exception of lithopone, which is yellow in IRFC. However, the lead shown in the XRF data suggests lead white as a possible pigment. Lead is present in all samples but XRF shows that the amount of lead is exceedingly higher in sample 1G than in most of the samples on page 1, which is evident in Figure 15 where all the samples on page 1 are presented. The red line represents sample 1G. The graph also shows that sample 1B (represented as the light blue line) contains high amounts of lead, indicating that the white layer under the green layer in sample 1B is also white lead. Additionally, the reflectance spectrum for sample 1G is a better match for lead white than for lithopone.

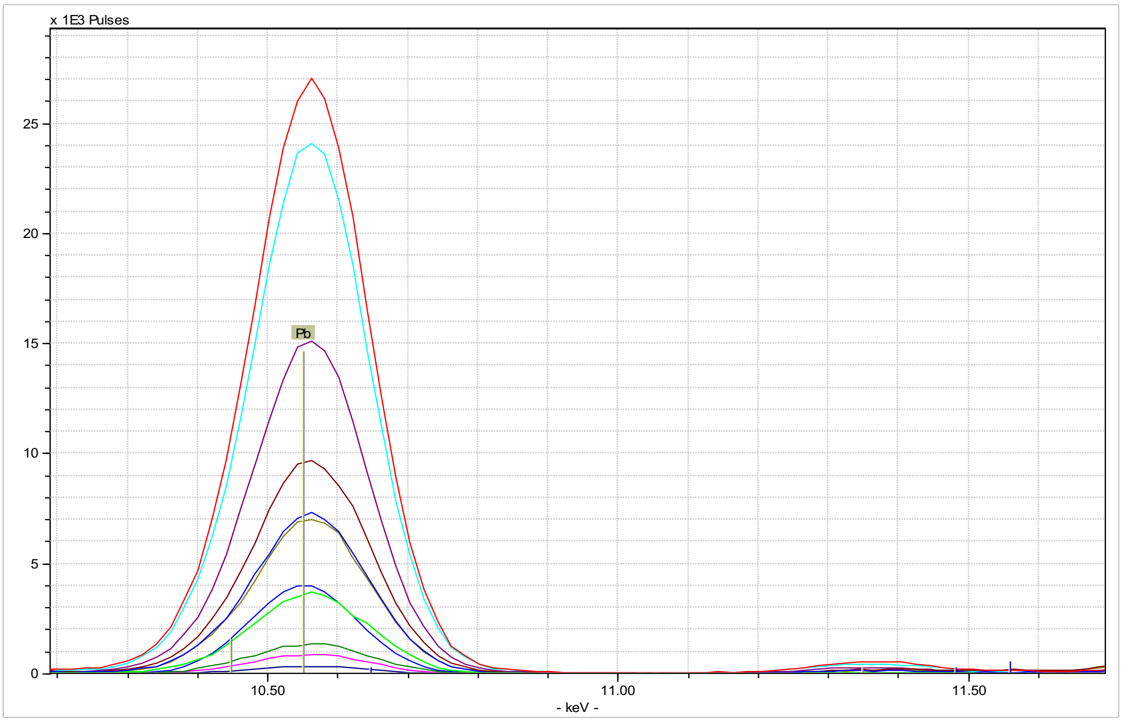

Figure 15. XRF spectra of the lead content of all samples on page 1. The red line represents the lead content of sample 1G. The light blue line represents the lead content of sample 1B.

5.1.7. Sample 1H, 1I, and 1J

1H is green and does not appear layered. It is dark in IR and UVR, does not emit fluorescence, and is black or purple in IRFC. If the IRFC is black, the flowchart suggests green earth; if it is purple, the flowchart suggests verdigris. Green earth contains iron, which is confirmed in the sample by XRF. Green earth has been used since ancient times and is still in use today (Feller 1986). 1J is also green and unlayered, and shows the same characteristics as 1H in the MSI results, with the exception of a light purple/brown color in IRFC. The purple color in IRFC indicates that the pigment is verdigris, but since XRF shows the presence of iron and not copper, this seems unlikely. The reflectance spectra for both 1H and 1J do not provide any characteristics, but when applying the first derivative, the match for green earth is more likely (Figure 16). No probable identification has been successful for sample 1H.

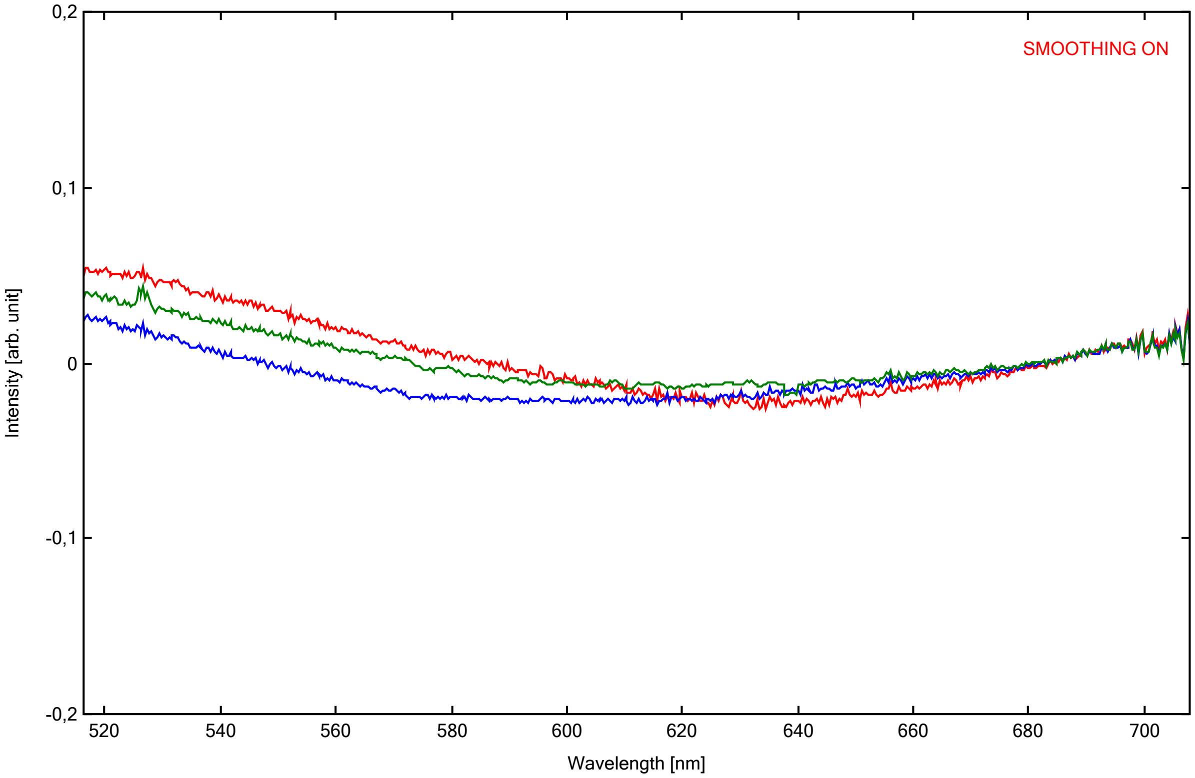

Figure 16. First derivative of reflectance spectra of sample 1J (red), 1H (blue), and green earth (green).

6. Discussion

6.1. Pigment Identification

Pigment identification proved to be quite difficult in this study due to small areas of analysis and mixed pigments. As suggested by Cosentino, it is necessary to use more than just one material-specific analytical method in order to reach an acceptable result. Even so, an identification is by no means a guarantee (Cosentino 2014b); in fact, there are very few cases where a definite identification can be made. This is especially true when working with objects of art where it can be difficult to find large areas of pure pigment. With that in mind, results from these kinds of studies should be seen as indications.

It was possible to provide most samples with a probable identification, some of which were more reliable than others. The pigments suggested by all three analytical methods are the most reliable, but even these are not conclusive results. Some pigments are recurring, for example vermillion, which makes them more reliable, even if they are not suggested by all three methods in all of the samples. In sample 1E, 4C, 6B, and 6E all methods suggest vermillion. In sample 1D vermillion is suggested by XRF and in 6F by MSI and XRF. Because the pigment is so frequently used, it is likely that it would be used for the red color in 1D and 6F as well. In addition, vermillion is one of the pigments presented in the list of paints purchased by Arosenius in Germany. All but one of the red samples are believed to be vermillion. However, samples 6E and 6F are probably a combination of vermillion and red lead, which is evident when applying the first derivative of the reflectance spectrum (Figure 17). These samples show an example of how application of the first derivative of reflectance spectra can be very useful, especially when reflectance spectra are very similar (Bacci 2000). For the remaining sample, 6A, both MSI and XRF suggest cadmium red, but the requirements for cadmium red are the same as for vermillion in the flowchart. The reflectance spectrum shows a peak at 600 nm. The spectra for cadmium red and vermillion are very similar; therefore, based on the UV-VIS, sample 6A could be either. However, based on the XRF results, cadmium red is a more probable identification.

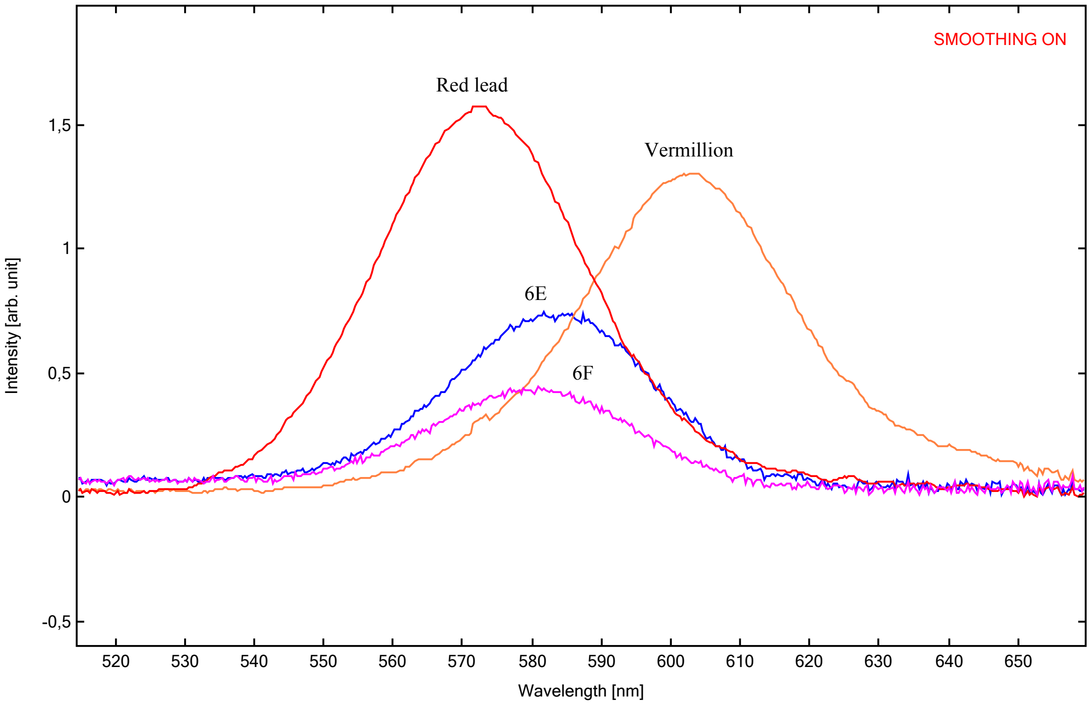

Figure 17. First derivative of reflectance spectra of sample 6E and 6F with red lead and vermillion.

A probable identification was not successful for two of the blue samples, 4E and 6G. Prussian blue is suggested by all three methods for sample 1F. Cobalt blue is suggested by all three methods for sample 2A, and is included in the list of pigments purchased by Arosenius. Sample 2E shows traces of both iron and cobalt, but the reflectance spectrum is a better match for Prussian blue. It is therefore only possible to state that it is either cobalt blue or Prussian blue, or a combination of both. Sample 5A has been identified as azurite, based on traces of copper detected by XRF and the correlating reflectance spectrum for azurite. Sample 6D is purple and could be a combination of a blue and a red pigment. Based on recurring pigments in previous results, these pigments could be vermillion and ultramarine. An average spectrum of the two pigments was made, which could be compared to the spectrum for 6D. The result was inconclusive; but, after adding red lead to the average spectrum, a probable identification was revealed (Figure 18). As previously discussed, a mixture of red lead and vermillion was most likely used in some of the red samples on page 6, so it is conceivable that the red colorant in sample 6D is a mixture as well.

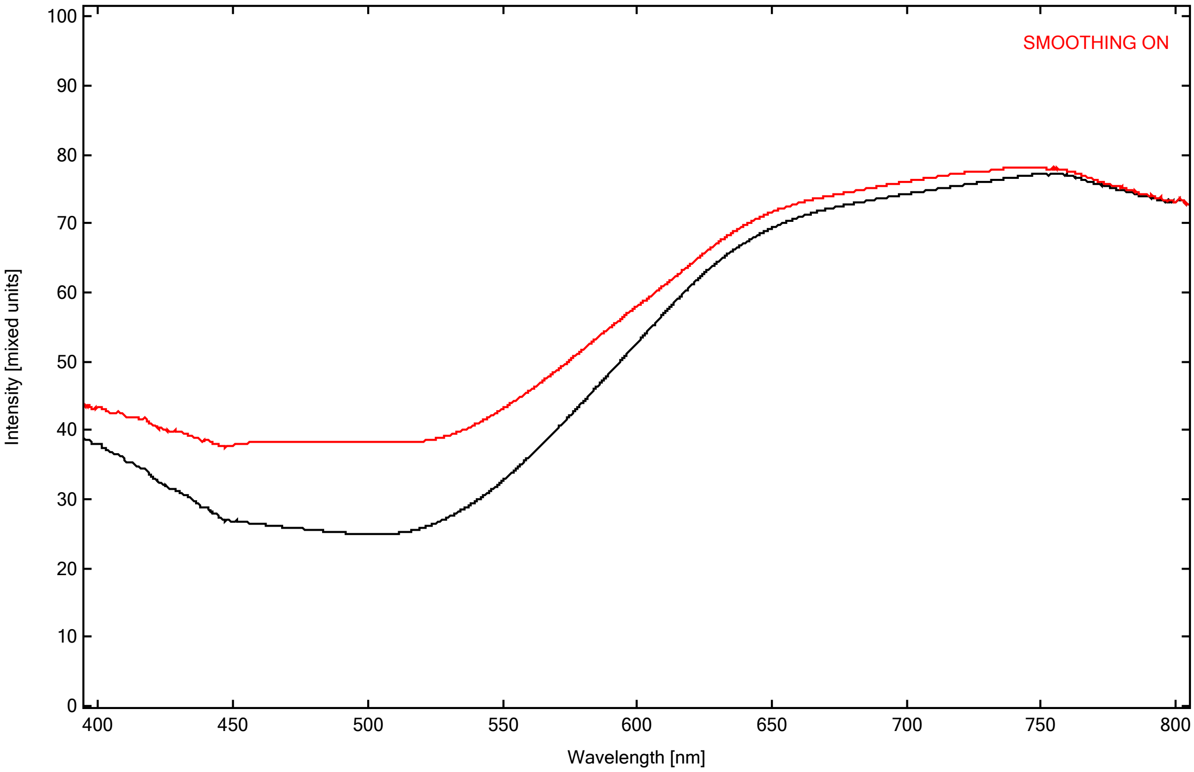

Figure 18. Reflectance spectra of sample 6D (purple line) and average of vermillion, red lead, and ultramarine (black line).

For two of the green samples, 1H and 1J, green earth has been assigned as the probable pigment, mainly due to the presence of iron. The presence of copper in sample 2B, and the results of the MSI, suggest verdigris or a copper resinate. 2C has been identified as cadmium green, based on the presence of cadmium and on a spectral peak at about 520 nm in the reflectance spectrum. The spectrum for cadmium green in the database shows a very distinctive peak at about 500 nm.

The brown pigments were difficult to identify, partly because the flowchart method did not provide any answers, and partly because brown pigments are often a combination of several colors. However, a probable identification could be provided for some of the brown samples, for example, 1D, which has already been mentioned. Samples 3A and 4B were suggested by XRF to be either raw or burnt sienna based on the presence of iron. The reflectance spectra are better matches with raw sienna than burnt sienna, which exemplifies how multiple analytical methods are useful in narrowing down the possible results. Sienna is also on the list of paints purchased by Arosenius. The yellow and white pigments were also difficult to identify, as neither of the samples have an identification that is suggested by all three methods. Two of the yellow samples, 4F and 6C, have been identified as gamboge, and the third sample, 4A, as cadmium yellow. The reflectance spectra for gamboge and cadmium yellow are very similar and are a match for all the samples, so the distinction between them is mainly based on the XRF results.

A probable identification was possible for 27 of 31 pigment samples. 15 different pigments have been identified, listed in Table 6. Six of the identified pigments, indicated with an asterisk, are included in the list of paints purchased by Arosenius in Germany, see Table 1.

Table 6. Identified pigments. Pigments with asterisk are included in the list of paints purchased by Arosenius.

Red	Blue	Green	Brown	Yellow	White
Cadmium red	Azurite	Cadmium green	Raw sienna*	Cadmium yellow*	Lead white*
Red lead	Cobalt blue*	Green earth		Cobalt yellow	
Vermillion*	Prussian blue	Verdigris		Gamboge	
	Ultramarine*				

For 12 of the samples, the probable identification was supported by all three methods. For 13 of the samples, the probable identification was supported by two of the methods. For two of the samples, the probable identification was supported by only one method. Four samples were not given any probable identification. There could be various explanations for this. The data from the analytical methods could be faulty, or the analyses may have been conducted improperly, due to human error. It is also possible that the samples are too small, or that the pigments in the samples are not included in the flowchart method or the spectral database.

Arosenius seemed to use the sketch book as a sort of palette, wiping off his brushes randomly. It is possible that he did not clean his brushes thoroughly after each use which means that there would be traces of multiple pigments in all or most samples. This could be an additional possible explanation for the presence of lead in all the samples, as well lead white being a filler pigment. It could also explain why mercury is present in many of the samples, since mercury-containing vermillion was used frequently.

6.2. Evaluation of Analytical Methods

The analysis methods used in this study have all been proven in various literature to be appropriate and useful methods for pigment identification. However, they can be problematic. As previously discussed, MSI is problematic when the samples in question are layered or mixed, which is often the case with art works. In this study, the flowchart method established by Cosentino (2014b), was used and was a useful tool in presenting a probable result. However, it is important to note that only 56 pigments are presented in the flowchart. It is possible that some of the pigments in this study are not included in the flowchart. An additional disadvantage is that brown pigments were not identifiable with MSI. When reviewing the images collected with MSI, it is also evident that the images are not ideal. The lighting was uneven and it was difficult to position the sketch book in a way that was safe for the object and at the same time produce ideal images. Figure 19 shows an additional problem with the images, which is a general distortion. The distortion could be a result of refocusing the camera between channels when conducting MSI analysis, which can lead to changing the size of the images (Informant 1). It could also be a result of the images not being taken in the exact same position. More time could have been spent on designing a better setup and on processing the images after analysis. It would have been beneficial to use the exact same spectral bands as in the flowchart in order to use the flowchart method to its fullest capacity. While most spectral bands were used, there are a few additional ones in the flowchart that were not used, which made identification somewhat difficult.

Another problematic issue with MSI, or specifically the flowchart method, is the complexity of interpreting colors. This is especially evident when the IRFC images are studied. To state that a sample is of the color purple is subjective and can differ depending on the interpreter of the image. The problem is not just limited to the IRFC images, but interpreting colors in general. This could be avoided by using a standardized color system.

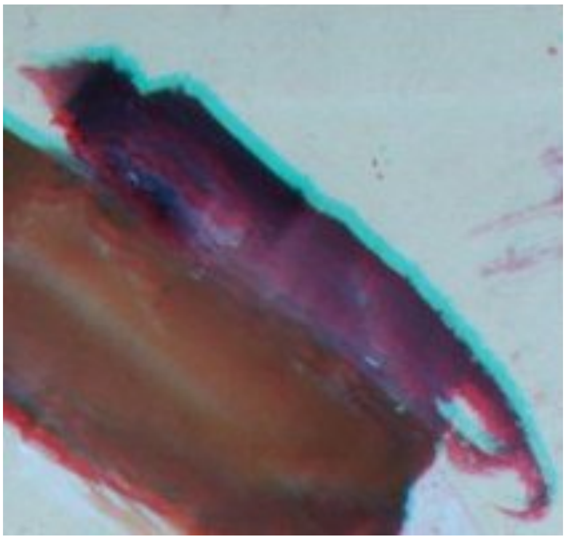
Figure 19. IRFC image of sample 1C.

The XRF spectrometer used in this study is intended for analysis of "low alloy steel, soil, mining, and metallurgical samples" (Olympus 2015). The settings might differ from those of a spectrometer intended for art analysis. A specific disadvantage of the spectrometer is that it is an in-contact instrument, which is not ideal for art objects. In this study, a protective window of Melinex was used, but it still poses a risk for the object, as it may be subjected to pressure of the spectrometer, especially if the pigments are unstable (Trentelman et al. 2012). Literature recommends using the same settings and conditions for all analyses (McGlinchey 2012). While the settings were the same during the course of the examination, the analyses were conducted on two separate days, which could mean that the conditions were not exactly the same.

XRF is relatively easy to use when conducting the analyses but it requires a lot of time to understand how to analyze the data and interpret the spectra. It requires experience to recognize when false negatives or false positives are produced, and which of the peaks are sum peaks. Because XRF only detects inorganic elements, the absence of elements can sometimes be an indication, for example, if a blue pigment shows no traces of iron, copper, or cobalt, it could indicate an organic blue, such as indigo. However, the absence of elements is never a reliable result and requires confirmation from at least one other method. It can be a way to rule out pigments though, for example if no iron is present in a blue sample, it is not possible for the sample to be Prussian blue, given that the analysis and data interpretation is correct. In this study, no identification has been made based solely on the absence of elements, but it has been used as an indication of how to proceed with the identification process.

The use of UV-VIS FORS as an analytical method proved to be very useful for several reasons. The instrumentation is easy to use, the results are straightforward, and the interpretation of the results does not require any advanced knowledge. The spectra can be used and interpreted as they are, and there are possibilities of using them to a greater extent, for example, by applying the first derivative. However, the spectral range used in this study was somewhat limited, as spectra was collected in the VIS and some of the UV range. A broader spectral range would have provided even more information, which could have been used to narrow down the possible identifications further, when needed.

Using several analytical methods is essential to properly identifying pigments, but sometimes leads to confusion. It can be very difficult to know which of the results is most reliable when the data provides contradictory results. To attain the most credible and plausible results, experience and logical reasoning are required. That being said, the methods used in this study were all important and provided complementing information.

6.3. Conclusion

This study has identified most of the pigments used in sketch book T 19/2001, by Ivar Arosenius. It has been proven that pigment identification was possible for the sketch book, using optical microscopy, XRF, UV-VIS FORS, and MSI. The study has also shown some of the problematic issues with conducting pigment identification of art objects, where the pigment areas can be small, multi-layered, of thin washes, and/or mixed. The analytical methods have been discussed and it has been stated that while they can be problematic, they are still very useful in providing the tools necessary for identifying pigments.

When conducting pigment identification, the context is important. Simply reviewing the results from the analytical methods is not enough, one must take into account the visual examination, pigment history and properties, as well as the historical knowledge about the object in question. It is important to consider what kind of object is examined. It is also difficult to present results of multi-instrumental pigment identification, because of the complexity of analyzing and interpreting the information obtained. However, considering the problematics surrounding pigment identification in objects of art, the pigment identification in this study is deemed successful.

6.4. Further Research

In this study, an identification for most of the pigments in sketch book T 19/2001 has been presented. To further strengthen the pigment identifications, analysis of reference pigments can be conducted with the same analytical methods. The results for the reference pigments can then be compared to the results in this study. The identification process can be applied to other works of art by Arosenius, as to broaden the knowledge of his use of pigments.

In order to obtain more reliable results, analyses with XRF and UV-VIS should be repeated more than once for each sample. From the UV-VIS data, the absorbance spectra as well as the reflectance spectra can be examined. An XRF-spectrometer intended for art, which requires no contact with the object, should be used. To improve the use of MSI, it would be of interest to collect images in all spectral bands used in the flowchart method. The flowchart would thus be easier to use.

7. Summary

The artist Ivar Arosenius (1878-1909) is an important figure in Swedish art history, and his distinctive artistry and untimely death has resulted in various portrayals and interpretations of the artist and his art. This vast and scattered body of information has led to a three-year research project called the Arosenius Project, which aims to gather and digitize information about the artist, and make it more accessible for researchers and the public. Little is known about the materials Arosenius used in his art, which is important information for the understanding of his artistry, and can be of use for future conservation treatments of his work.

By using non-invasive and non-destructive analytical methods, this study aimed to investigate and identify the pigments Arosenius used in one of his sketch books, and how well the chosen analytical methods perform in pigment identification for the chosen book. The sketch book used in this study (inventory number T 19/2001) belongs to the Arosenius collection at the Gothenburg Museum of Art (GKM). The sketch book is dated 1908 and has six pages with 31 areas of paint in total. The sample areas vary in color, size, and thickness, and are often overlapping. Of the twelve sketch books in the Arosenius collection at GKM, the object was selected as it contained the most areas of analysis.

This study has used optical microscopy, X-ray fluorescence (XRF), ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS), and multispectral imaging (MSI) to identify the pigments. The analytical methods are both non-invasive and non-destructive. Optical microscopy provides the basic information that is necessary to move forward with the identification, such as color and possible layering and/or mixing of pigments. XRF provides elemental information about inorganic elements; UV-VIS FORS provides the reflectance spectra of the samples; and MSI provides images in various spectral bands. The study has also used a list of paints purchased by Arosenius in Germany in 1907, as an indication of the pigments Arosenius might have preferred. Literature concerning pigment composition and history was reviewed, in order to further confirm the identifications presented in the study.

The experimental part of this study took place at GKM. The results from the methods were analyzed and interpreted, and when possible, a probable identification was presented, taking into account the historical context of the proposed pigments. This study presents a probable identification for 27 of the 31 pigment samples. 15 different pigments are identified: vermillion, red lead, cadmium red, ultramarine, Prussian blue, cobalt blue, azurite, green earth, verdigris, cadmium green, raw sienna, cadmium yellow, gamboge, cobalt yellow, and lead white. Six of the identified pigments (vermillion, ultramarine, cobalt blue, sienna, cadmium yellow, and lead white) are included in the list of paints purchased by Arosenius in Germany.

The pigment identification was considered successful, and the analytical methods were deemed useful in providing the tools needed to conduct pigment identification. However, complications arise when examining an object of art where the areas of analysis can be quite small and the pigment samples layered, of thin washes, and/or mixed. This study emphasizes that the identifications should be seen as indications. Some of the identifications were more reliable than others, primarily those suggested by all three analytical methods. For future research, a comparison with reference pigments can be conducted, to further strengthen the identifications.

The results of this study will contribute to the Arosenius Project and to the general information about Arosenius' artistry and his use of materials. It can be used as a pilot study for similar multi-instrumental analytical studies for additional works of art by Arosenius. It is also an example of how conservation science can be of help in conservation and art historical research.

8. Sammanfattning

Konstnären Ivar Arosenius (1878-1909) är en viktig del i den svenska konsthistorien, och hans särpräglade konst och tidiga död har resulterat i mångsidiga avbildningar och tolkningar av konstnären och hans konst. Detta har lett till ett treårigt forskningsprojekt, Aroseniusprojektet, som ämnar samla och digitalisera information om konstnären och göra det mer tillgängligt för forskare såväl som allmänheten. Det finns väldigt lite information om vilka material som Arosenius använde, vilket är en viktig beståndsdel i förståelsen för han konstnärskap. Materialinformation kan även vara viktigt för framtida konserveringsåtgärder på verk av Arosenius.

Denna studie ämnar undersöka och identifiera vilka pigment som Arosenius använde i en av sina skissböcker, genom att använda icke-invasiva och icke-destruktiva analytiska metoder. Studien undersöker också hur väl de analytiska metoderna är lämpade för identifikation av pigment för det valda objektet. Skissboken som används i denna studie, med inventarienummer T 19/2001, tillhör Aroseniussamlingen som finns på Göteborgs Konstmuseum (GKM). Boken är daterad 1908 och har sex sidor med 31 områden med färg. Områdena varierar i färg, storlek och tjocklek och överlappar ofta varandra. Boken, som är en utav tolv skissböcker som finns i Aroseniussamlingen, valdes på grund av att den hade flest färgområden.

Studien använder sig av mikroskopi, X-ray fluorescence (XRF), ultraviolet-visible fiber optic reflectance spectroscopy (UV-VIS FORS) och multispectral imaging (MSI) för att identifiera pigmenten. Alla metoder är icke-invasiva och icke-destruktiva. Mikroskopi bidrar med den grundläggande informationen om pigmenten som krävs för att gå vidare med identifikationen, såsom färg, eventuella skikt och/eller blandningar av pigment. XRF undersöker den kemiska sammansättningen av oorganiska ämnen. Med UV-VIS FORS kan reflektans spektra av färgerna i skissboken erhållas, och MSI bidrar med bilder tagna i olika spektrala band, som användes för att vidare karakterisera pigmenten. Studien använde även en lista med färger, som Arosenius köpte i Tyskland år 1907, som en indikation på vilka pigment han kan ha föredragit. Litteratur om pigment har granskats för att erhålla information om olika pigments historia och kemisk sammansättning.

Den experimentella delen av studien tog plats på GKM. Resultaten analyserades och tolkades och när det var möjligt presenterades en trolig identifikation, med den historiska kontexten av de föreslagna pigmenten tagen i beaktande. Studien presenterar en trolig identifikation för 27 av de 31 områdena av färg. 15 olika pigment är identifierade: vermillion, blyrött, kadmiumrött, ultramarin, Pariserblått, koboltblått, azurit, terra verte, verdigris, kadmiumgrönt, sienna, kadmiumgult, gummigutta, koboltgul och blyvitt. Sex av de identifierade pigmenten (vermillion, ultramarin, koboltblått, sienna, kadmiumgult och blyvitt) finns i listan av färger som inhandlades av Arosenius i Tyskland.

Identifikationen av pigment anses lyckad och de analytiska metoderna bedöms som användbara för pigmentidentifikation. Dock uppstår problem när konstobjekt undersöks, där mätpunkterna för analys är små, och pigmentlagren kan vara tunna, blandade, och/eller bestå av flera lager. Resultaten av denna studie bör endast ses som indikationer. Vissa resultat är mera pålitliga än andra, särskilt de där alla tre analysmetoder leder till samma resultat. För vidare forskning skulle en jämförelse med referenspigment utföras, för att stärka identifikationerna.

Resultaten av denna studie kommer att bidra till Aroseniusprojektet och till vidare forskning om Arosenius konstnärskap och materialval. Studien kan ses som pilotstudie för liknande multi-instrumentella analytiska studier för andra konstverk av Arosenius. Det är även ett exempel i hur konserveringsvetenskap kan vara ett hjälpmedel i konsthistorisk forskning och forskning i konservering.

Tables and Figures

Tables

Tables in Appendix

Figures

All photos taken by Victoria Skalleberg if nothing else indicated. All illustrations made by Victoria Skalleberg if nothing else indicated.

Figures in Appendix

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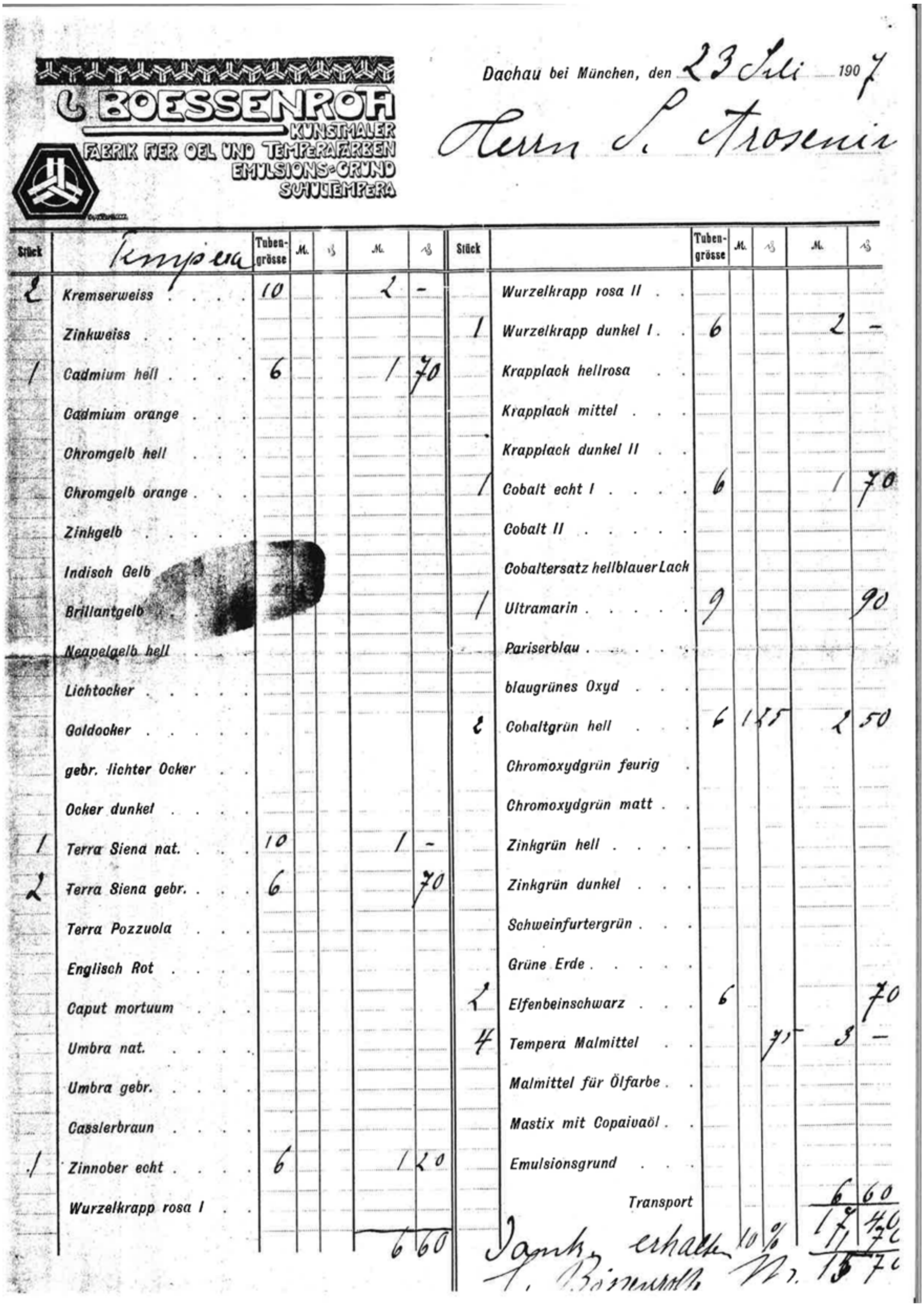
Appendix

Appendix 1. List of Paints



C. BOESSENROTH
KUNSTMALER
FABRIK FÜR OEL UND TEMPERAFARBEN
EMULSIONS-GRUND
SCHULTEMPERA

Dachau bei München, den 23 Juli 1907

Herrn I. Arosenius

Stück	Tempera	Tuben-grösse	M.	₰	M.	₰	Stück		Tuben-grösse	M.	₰	M.	₰
2	Kremserweiss	10			2	–		Wurzelkrapp rosa II					
	Zinkweiss						1	Wurzelkrapp dunkel I	6			2	–
1	Cadmium hell	6			1	70		Krapplack hellrosa					
	Cadmium orange							Krapplack mittel					
	Chromgelb hell							Krapplack dunkel II					
	Chromgelb orange						1	Cobalt echt I	6			1	70
	Zinkgelb							Cobalt II					
	Indisch Gelb							Cobaltersatz hellblauer Lack					
	Brillantgelb						1	Ultramarin	9				90
	Neapelgelb hell							Pariserblau					
	Lichtocker							blaugrünes Oxyd					
	Goldocker						2	Cobaltgrün hell	6	1	25	2	50
	gebr. lichter Ocker							Chromoxydgrün feurig					
	Ocker dunkel							Chromoxydgrün matt					
1	Terra Siena nat.	10			1	–		Zinkgrün hell					
2	Terra Siena gebr.	6				70		Zinkgrün dunkel					
	Terra Pozzuola							Schweinfurtergrün					
	Englisch Rot							Grüne Erde					
	Caput mortuum						1	Elfenbeinschwarz	6				70
	Umbra nat.						4	Tempera Malmittel			75	3	–
	Umbra gebr.							Malmittel für Ölfarbe					
	Casslerbraun							Mastix mit Copaivaöl					
1	Zinnober echt	6			1	20		Emulsionsgrund					
	Wurzelkrapp rosa I							Transport				6	60
												17	40
					6	60		Dank erhalten		10 %		1	70
								C. Bössenroth		Mk.		15	70

Figure I. List of paints, purchased by Arosenius in Germany (Göteborgs Konstmuseum 2017).

Appendix 2. Page 1-6 with Areas of Analysis

Figure II. Page 1. Sample 1A-1J.

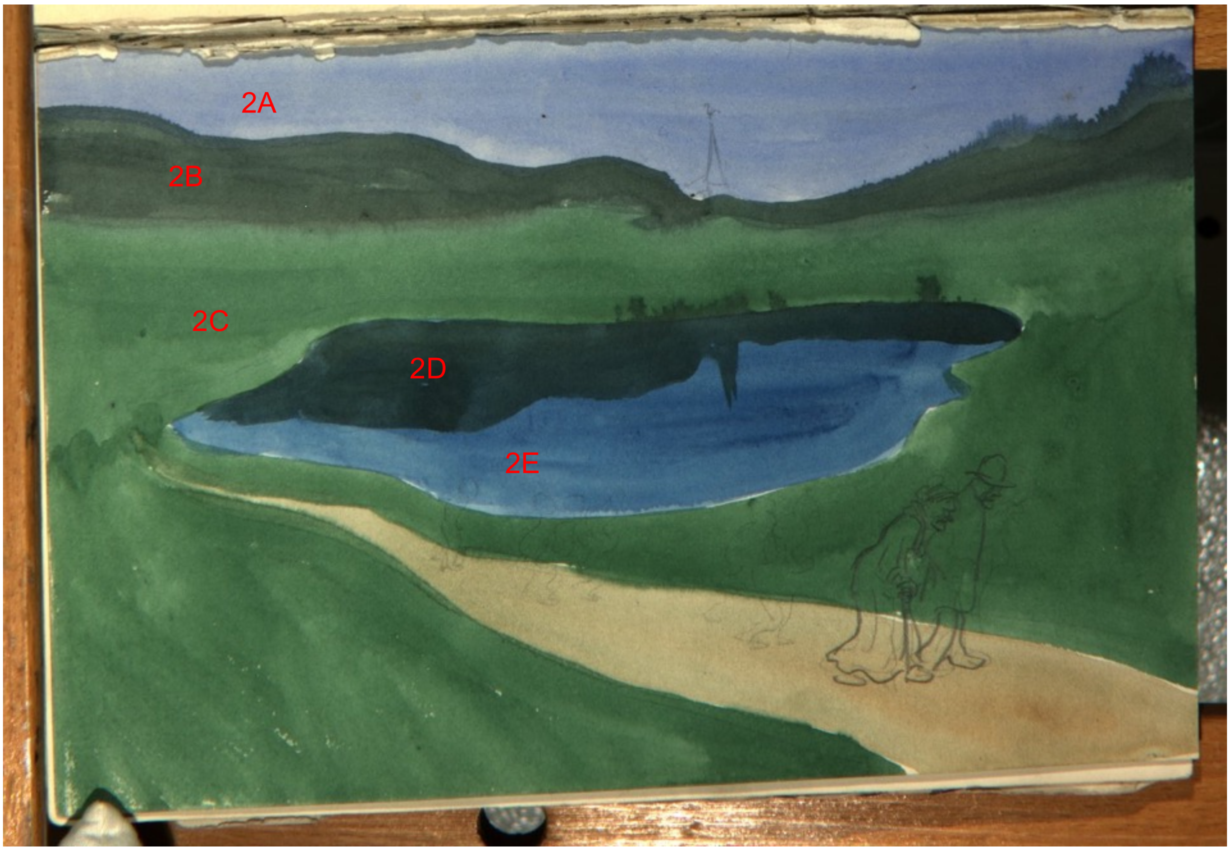


Figure III. Page 2. Sample 2A-2E.

Figure IV. Page 3. Sample 3A.

Figure V. Page 4. Sample 4A-4G.

Figure VI. Page 5. Sample 5A.

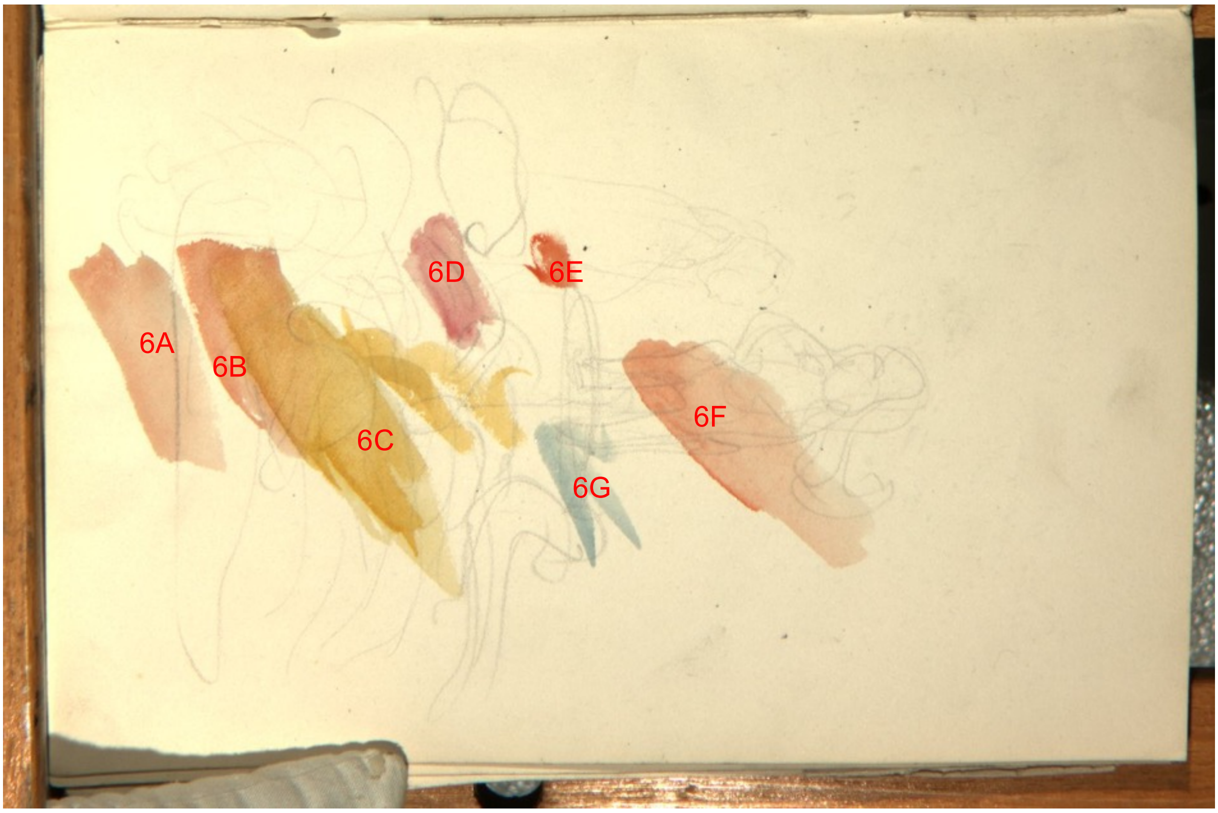
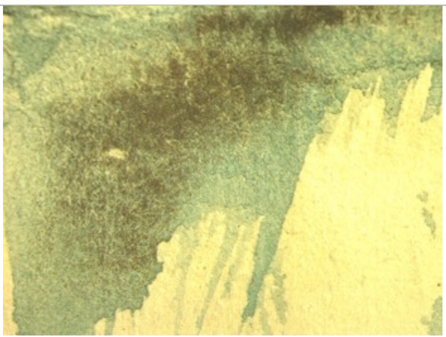
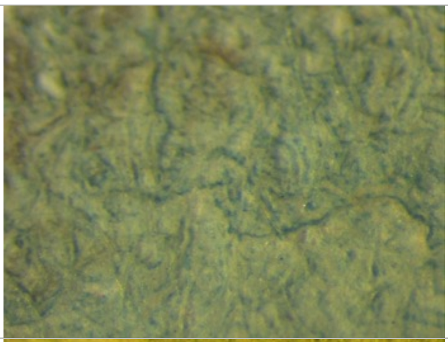
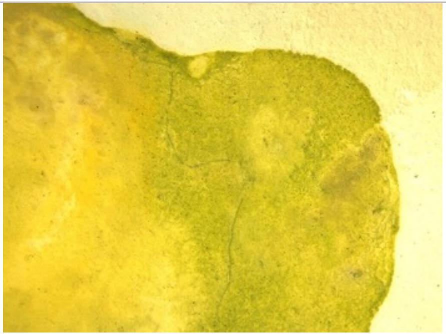
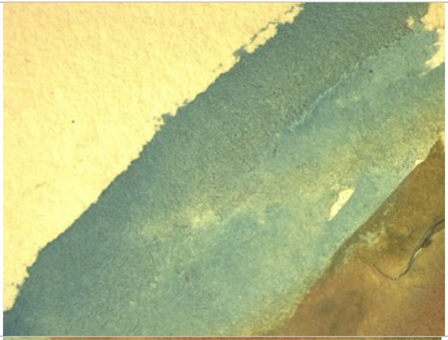
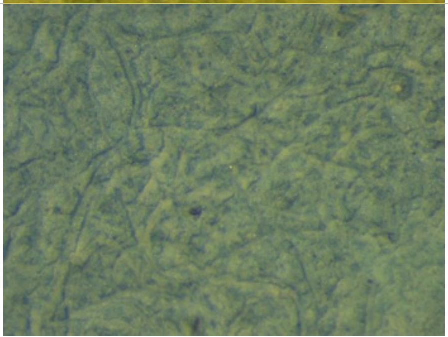
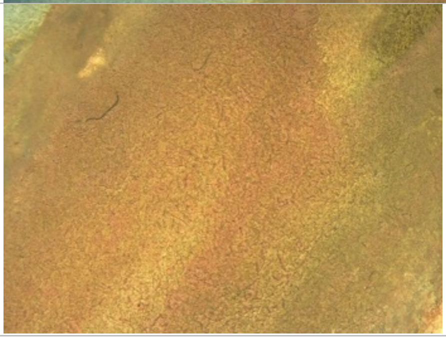
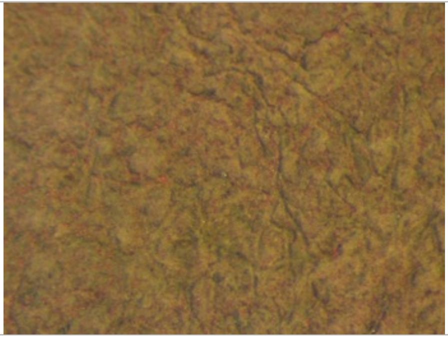
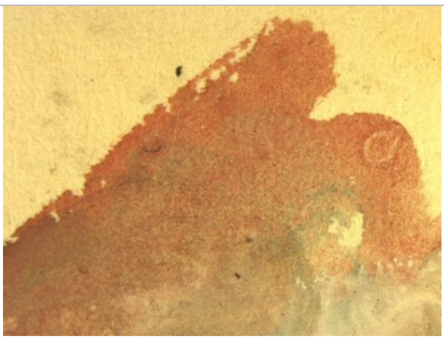
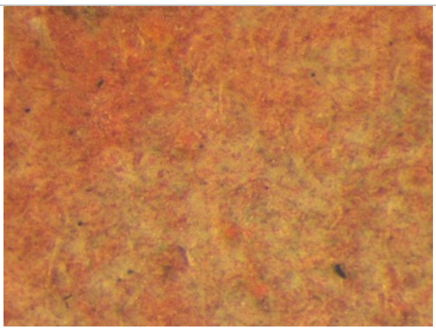
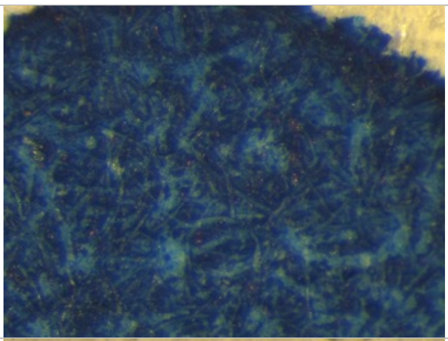
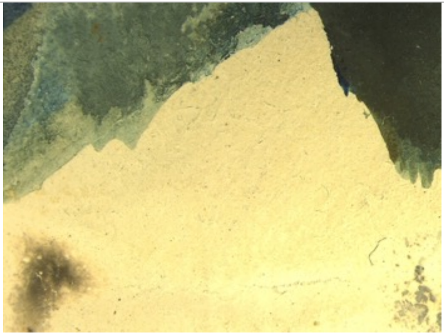
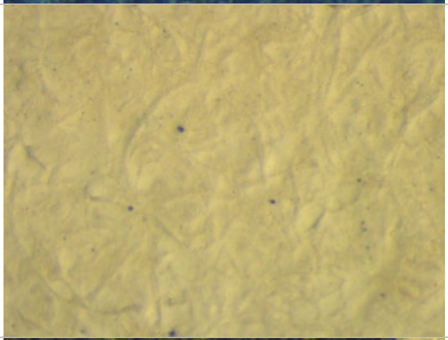
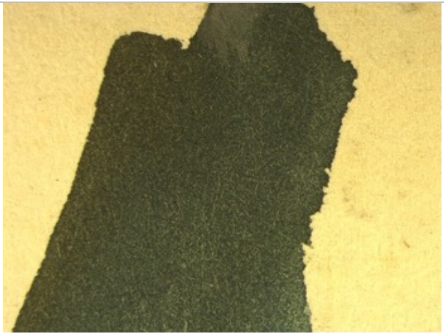
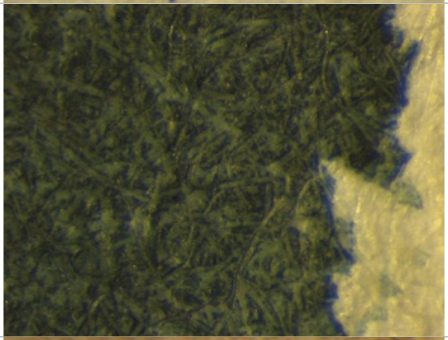
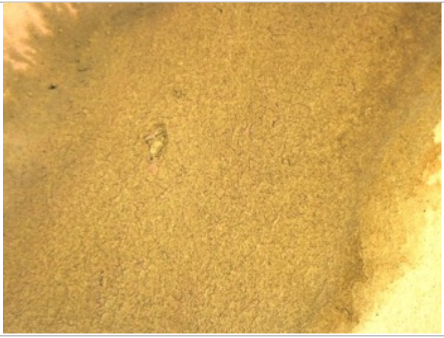
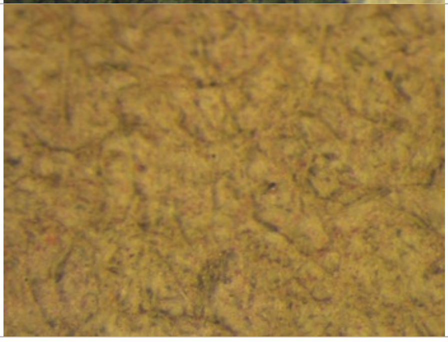


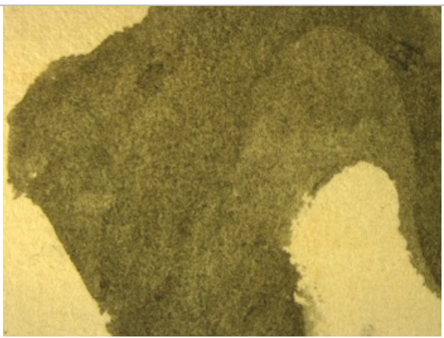
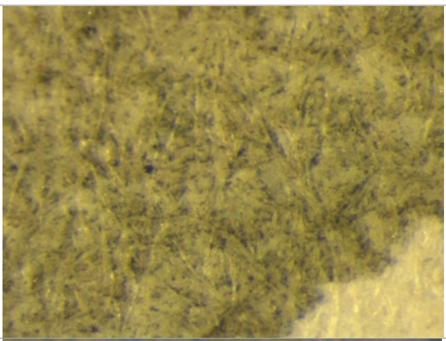
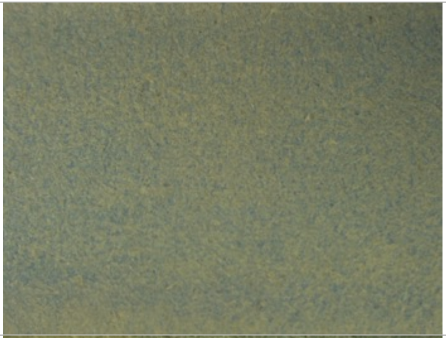
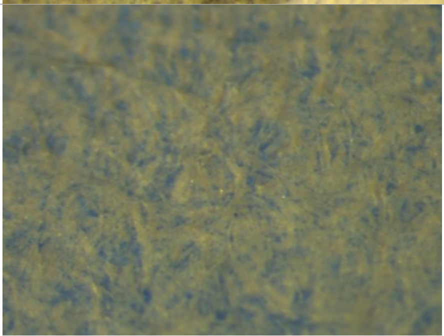
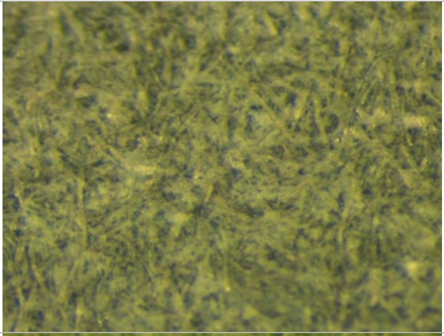
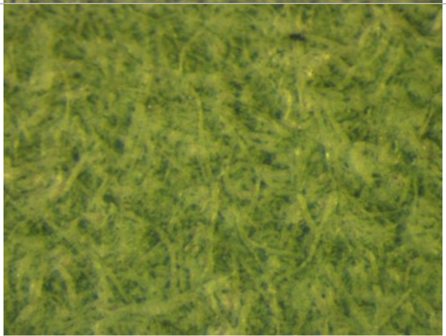
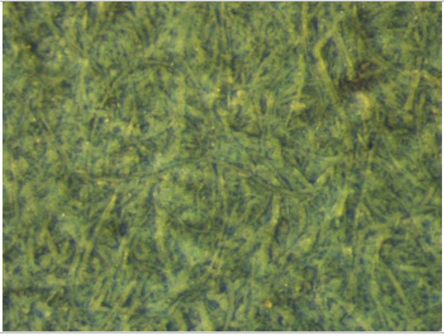
Figure VII. Page 6. Sample 6A-6G.

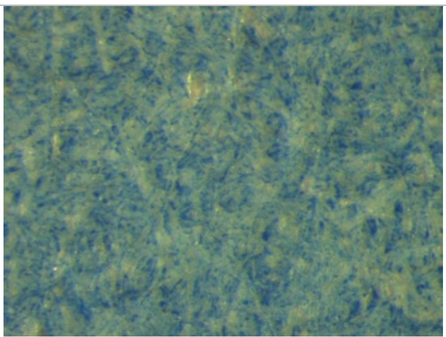
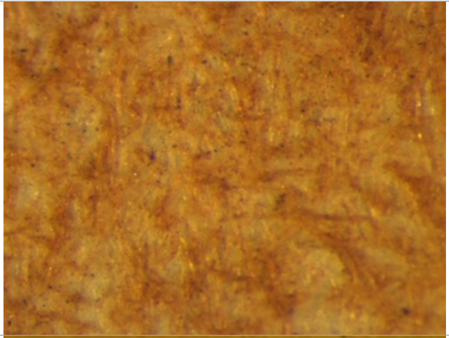
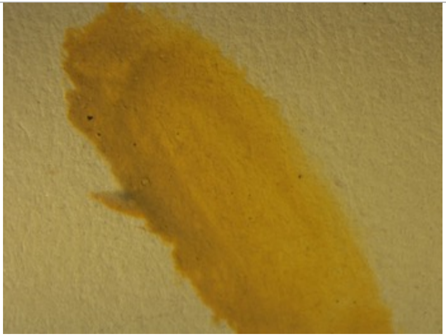
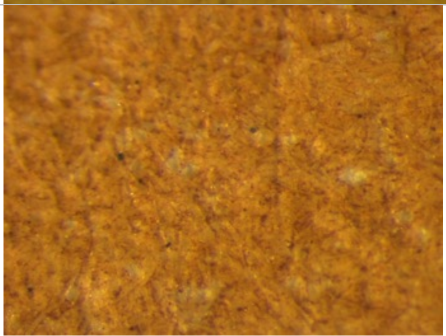
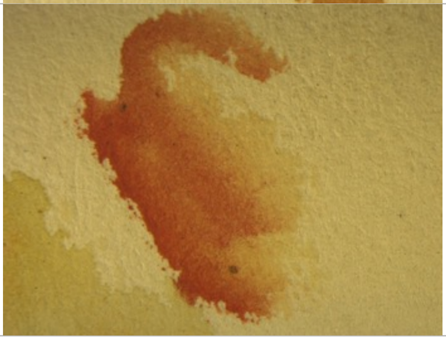
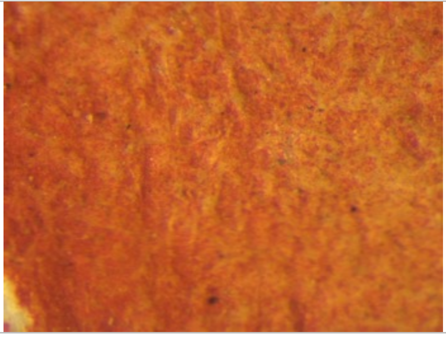
Appendix 3. Microscopy Images

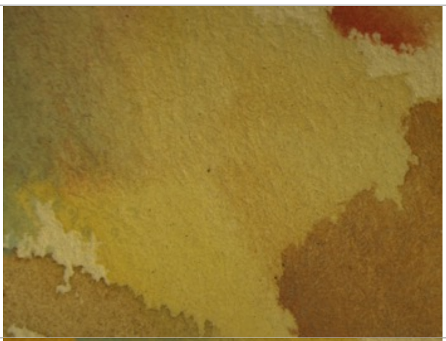
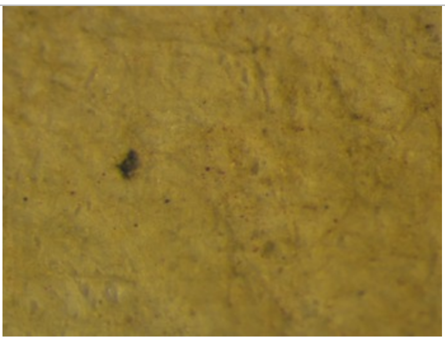
Table I. Microscopy images of the areas of analysis, taken at the magnification of 75x and 60x.

Sample ID	Magnification 7.5x	Magnification 60x
1A		
1B		
1C		
1D		

1E		
1F		
1G		
1H		
1I		

1J		
2A		
2B		
2C		
2D		

2E		
3A		
4A		
4B		
4C		

4D		
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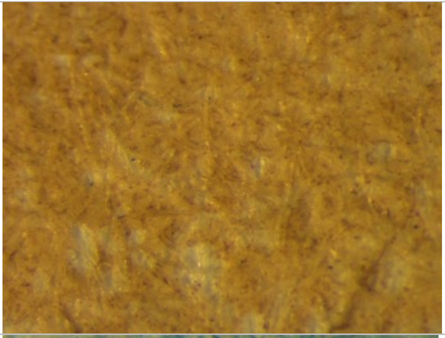
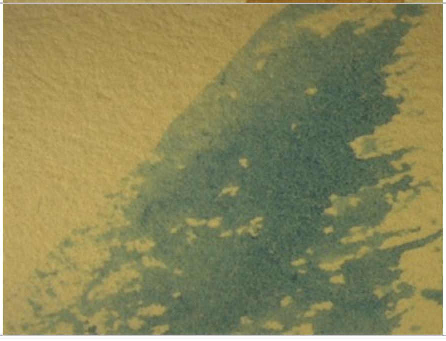
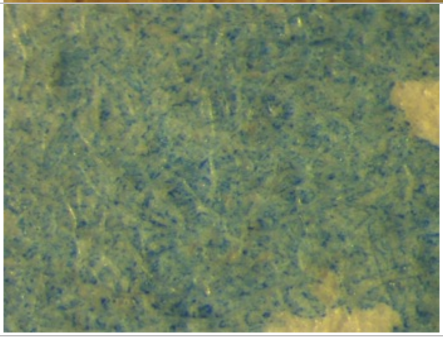
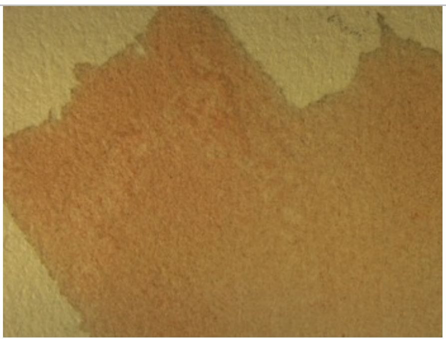
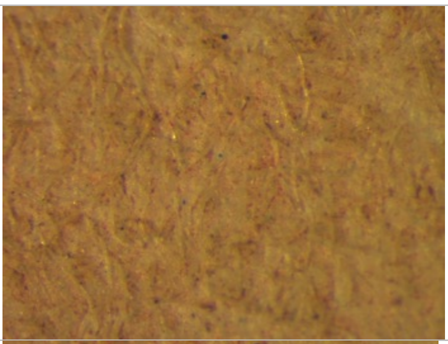
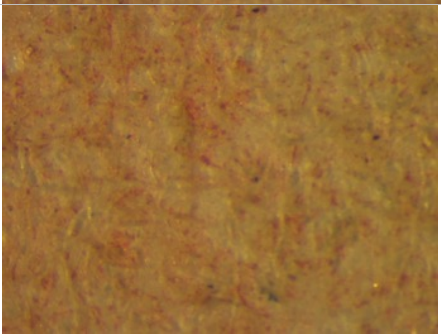
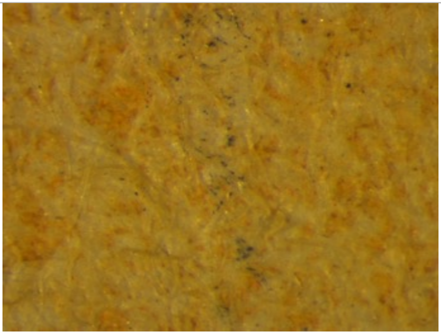
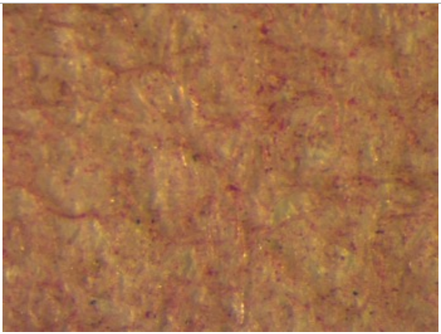
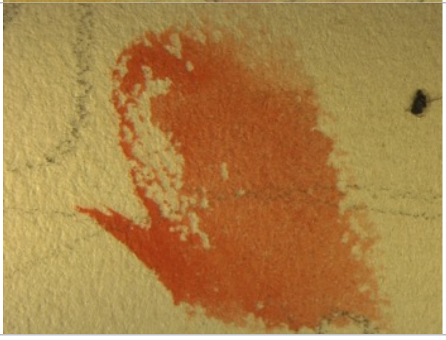
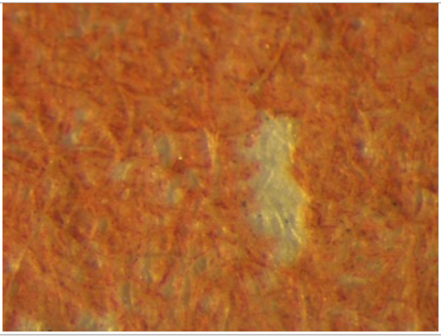
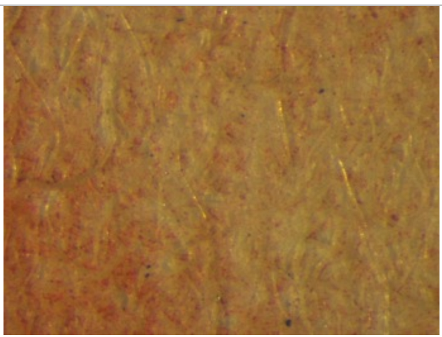
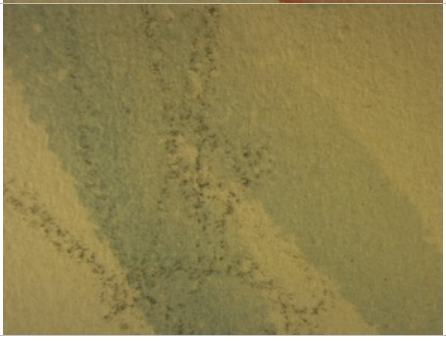
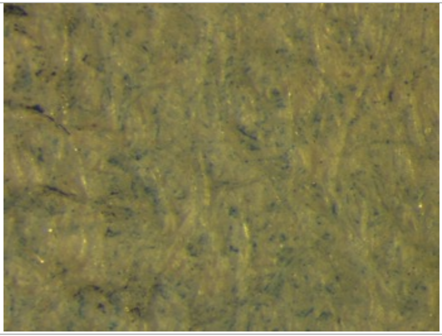
4F		
4G		
5A		

6A		
6B		
6C		
6D		
6E		

6F		
6G		

Appendix 4. MSI Results: Spectral Images

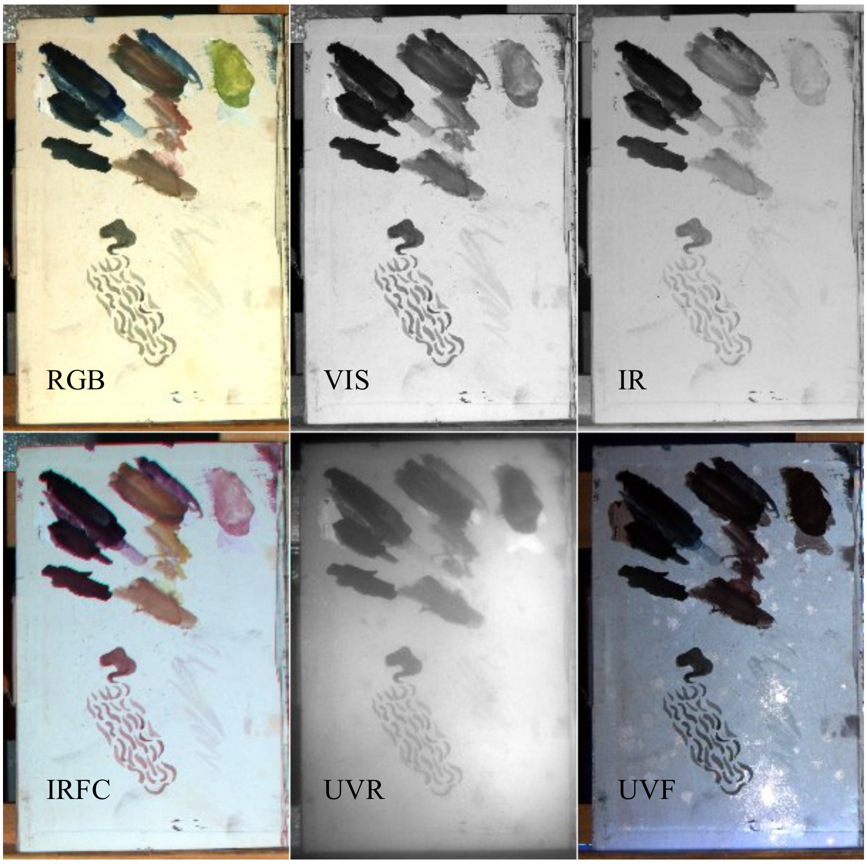


Figure VIII. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 1.

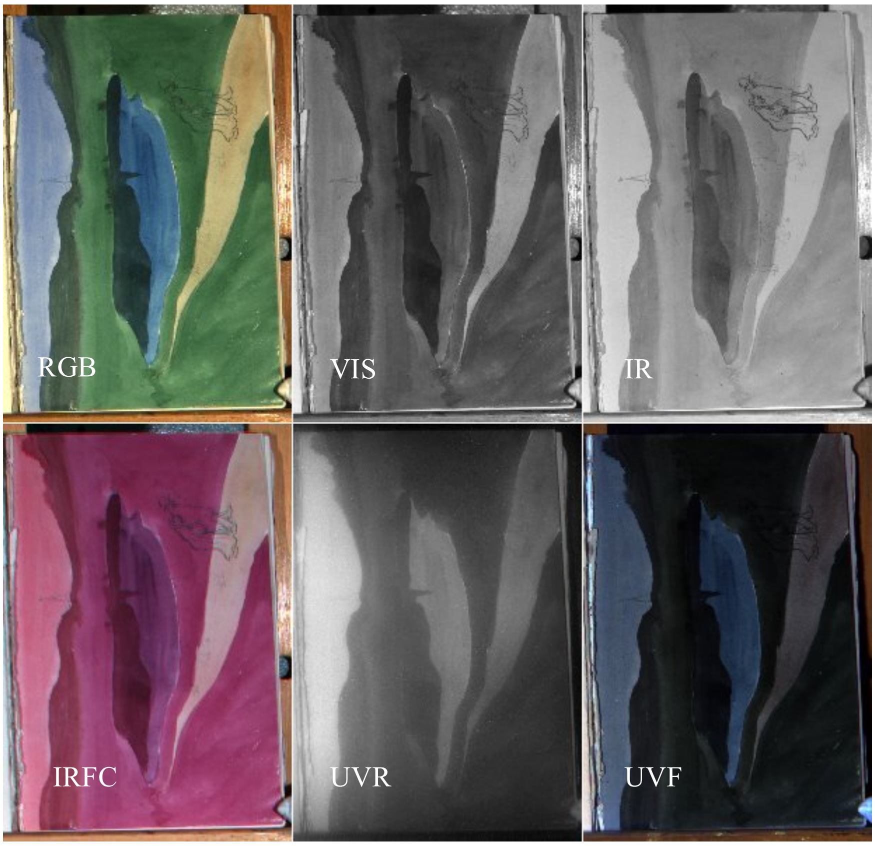


Figure IX. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 2.

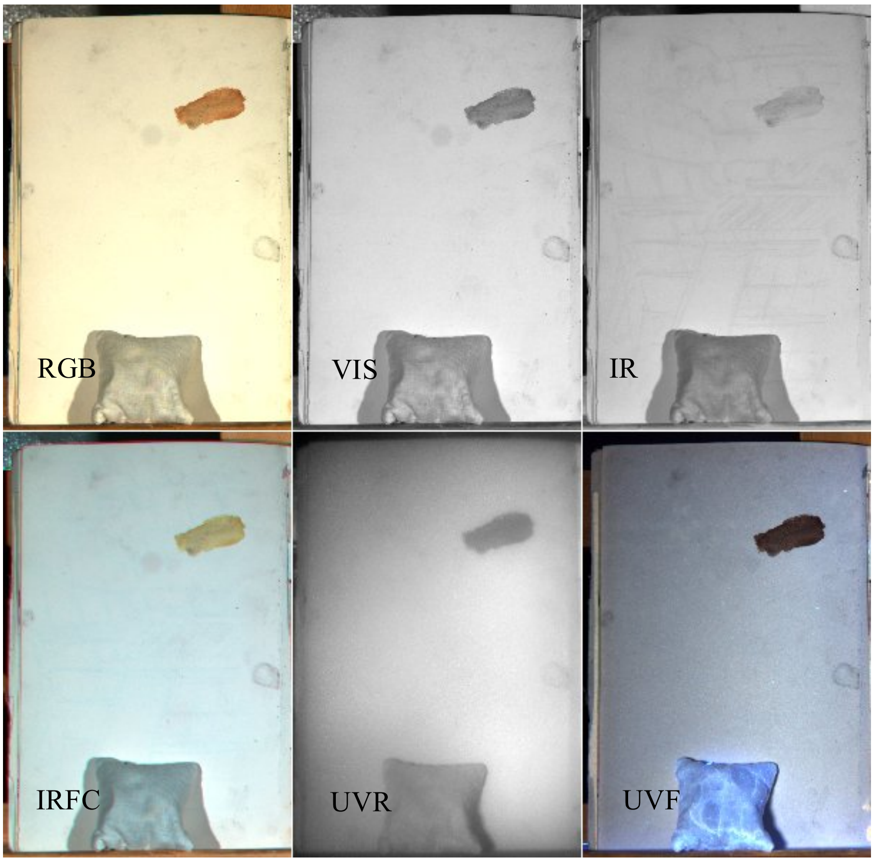


Figure X. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 3.

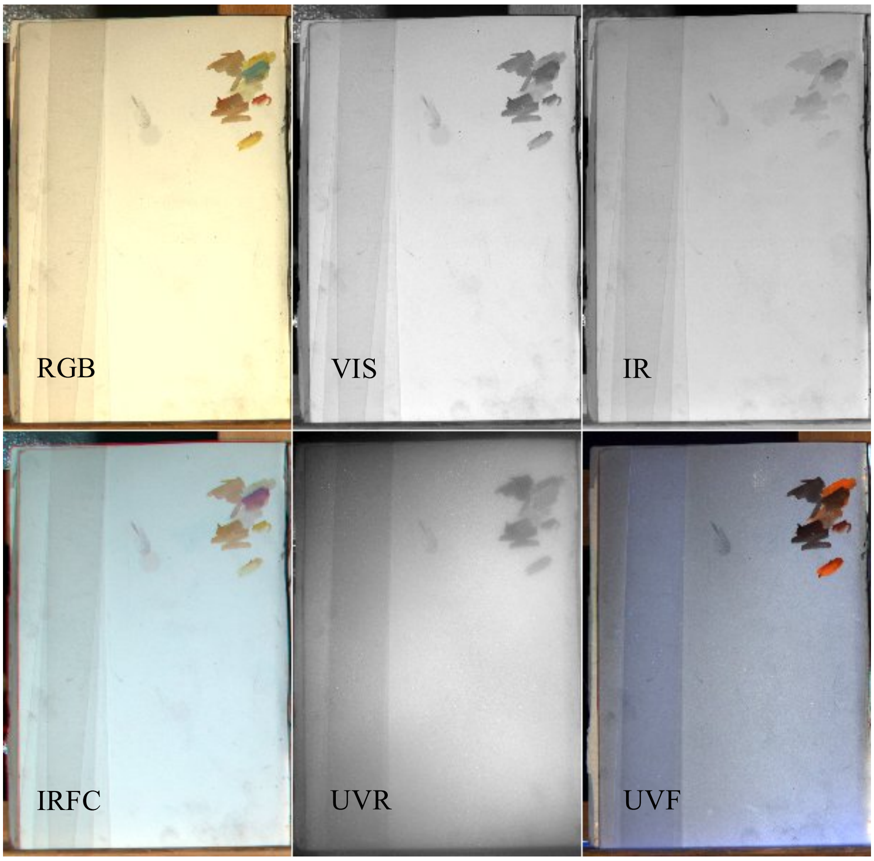


Figure XI. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 4.

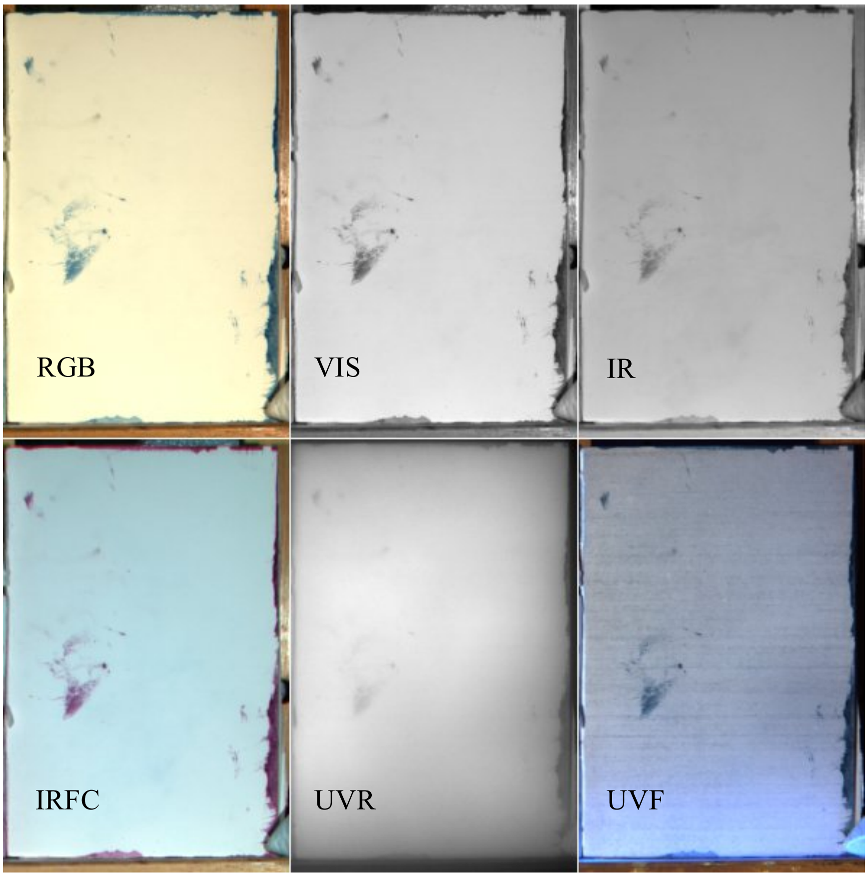


Figure XII. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 5.

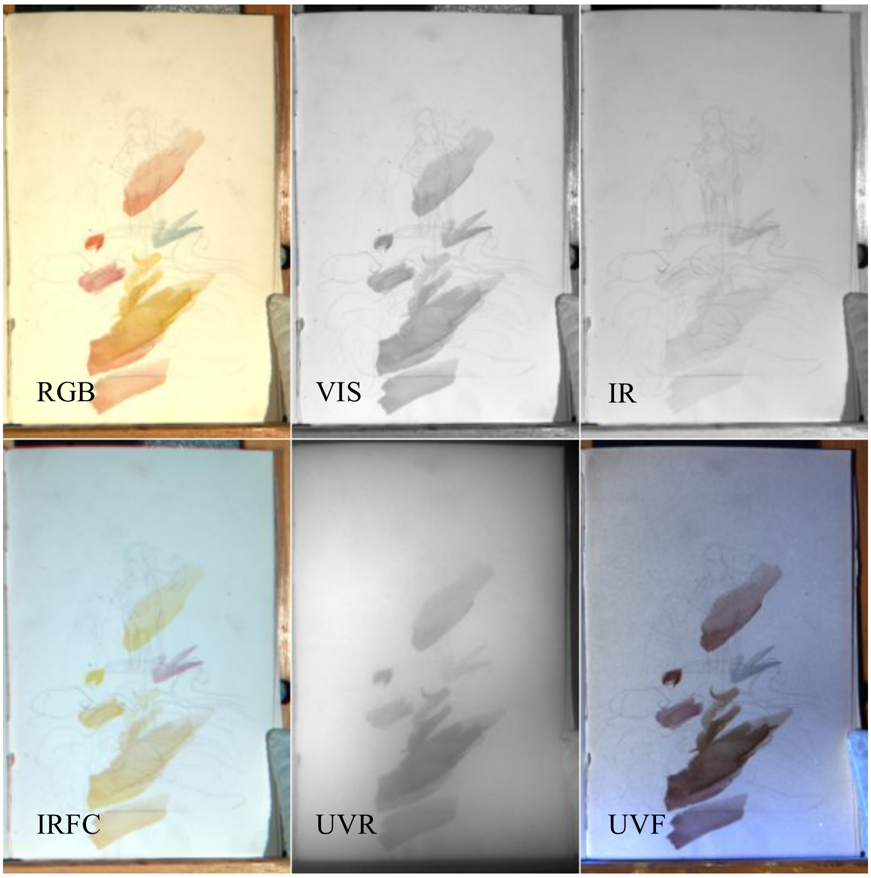
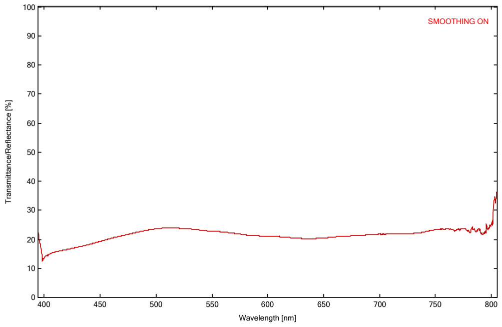
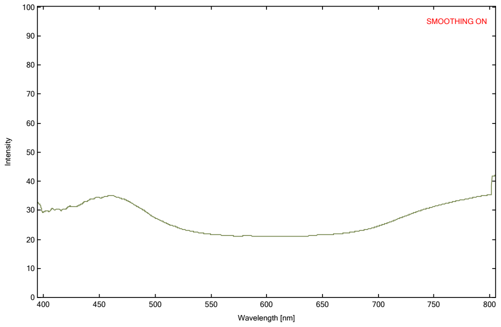
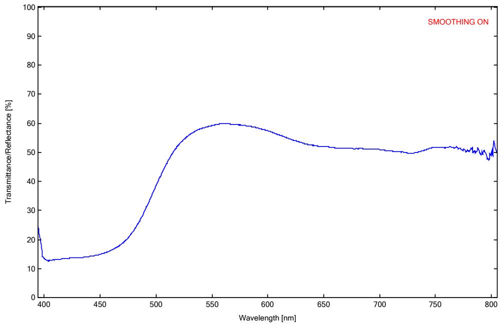
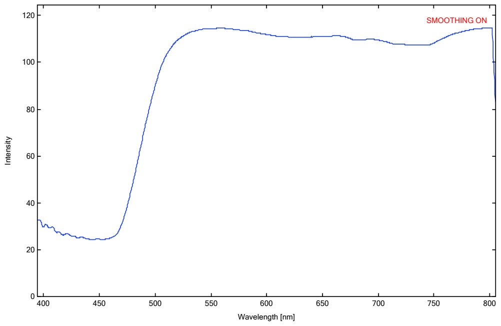
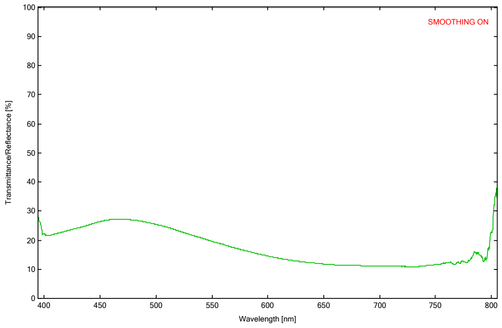
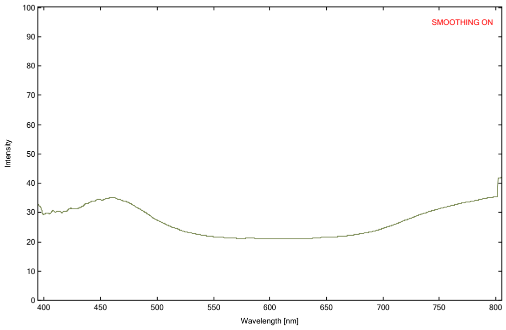
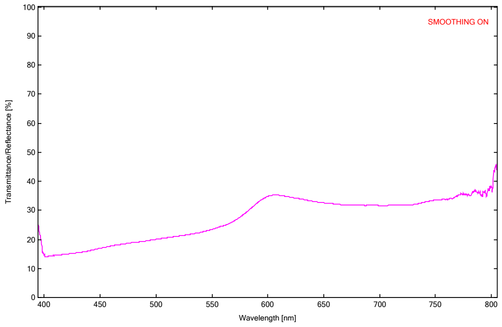
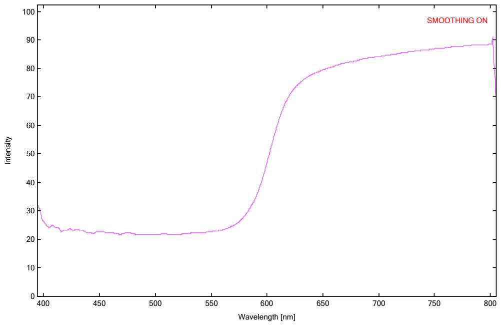


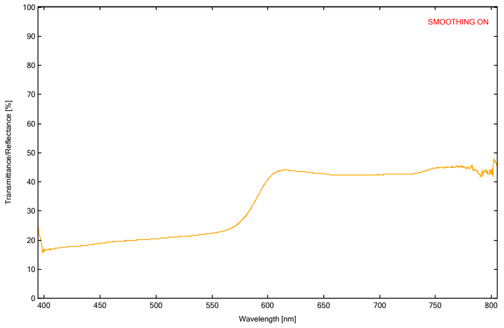
Figure XIII. Montage of MSI images (RGB, VIS, IR, IRFC, UVR & UVF) of page 6.

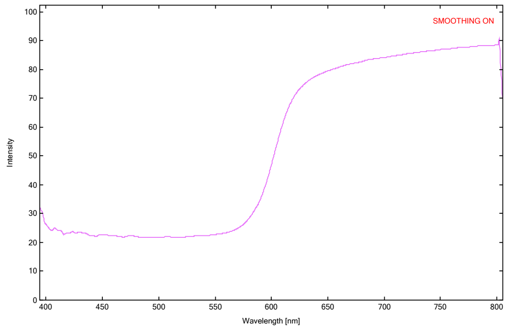
Appendix 5. UV-VIS FORS Results: Reflectance Spectra and Reference Spectra

Table II. Reflectance spectra and reference spectra. Reference spectra collected from Cosentino (2014a).

ID	Reflectance spectra	Reference spectra
1A		 Ultramarine
1B		 Cadmium yellow
1C		 Ultramarine
1D		 Vermillion

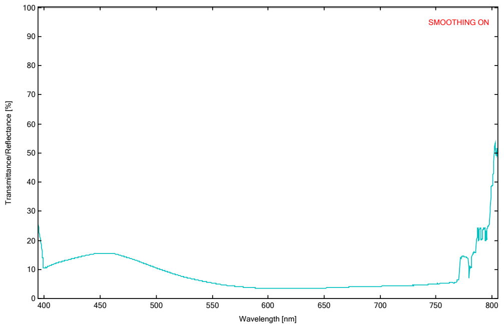
1E

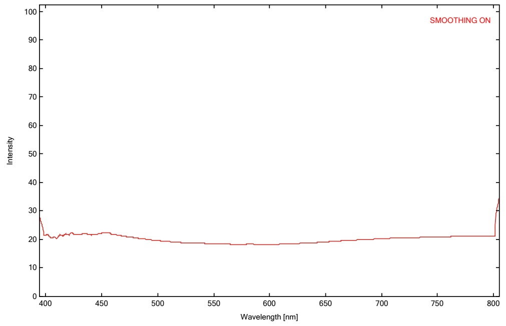




Vermillion

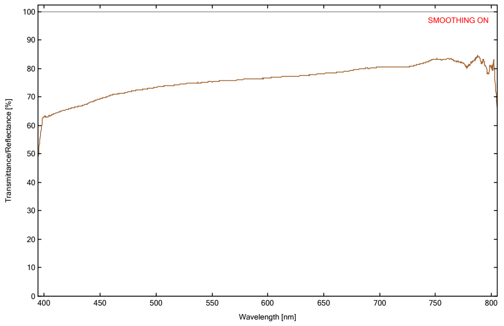
1F

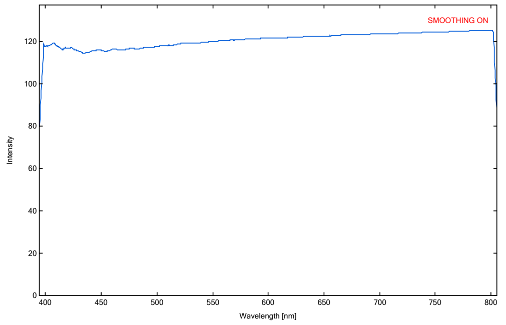




Prussian blue

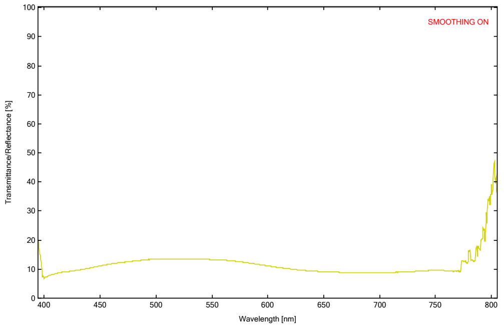
1G

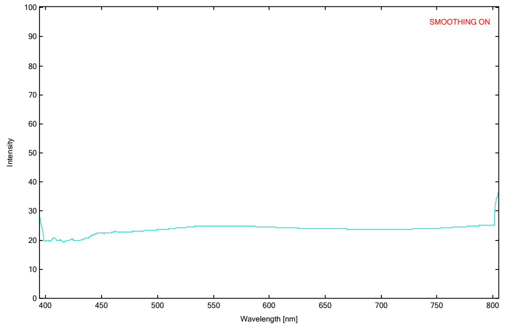




Lead white

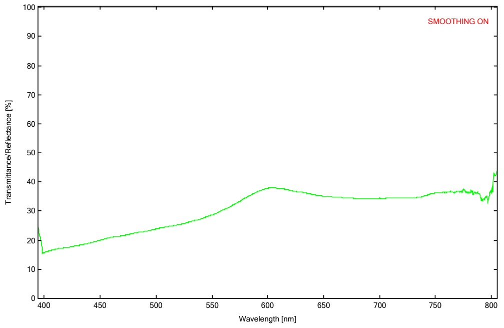
1H



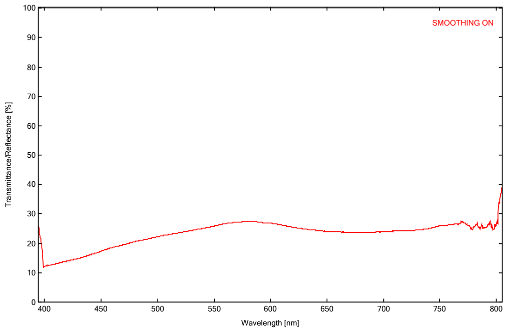
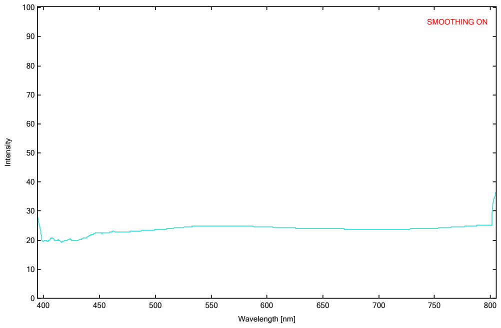
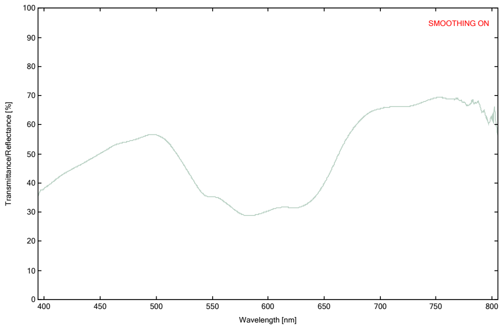
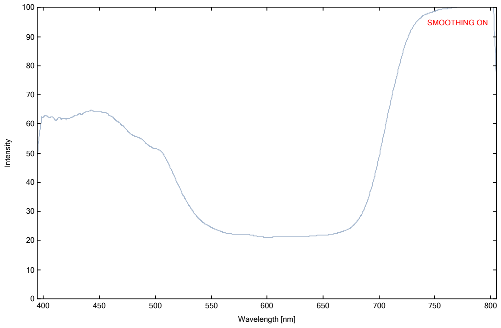
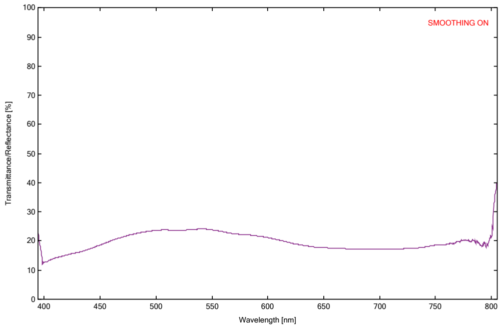
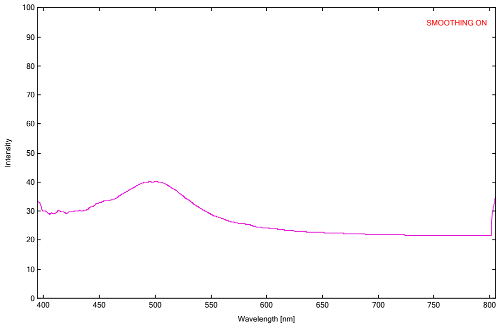
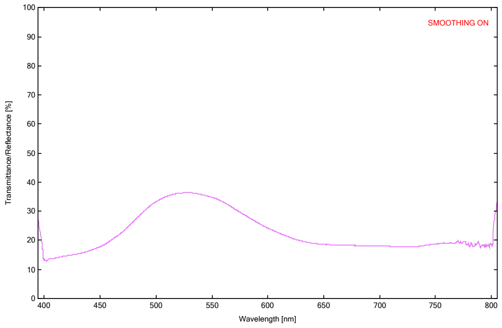
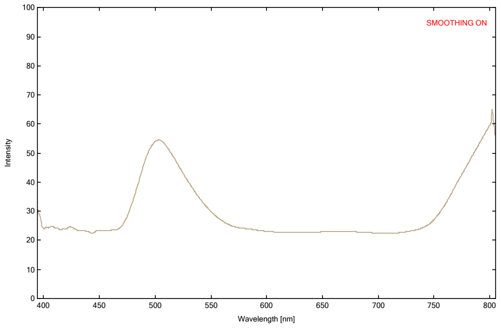
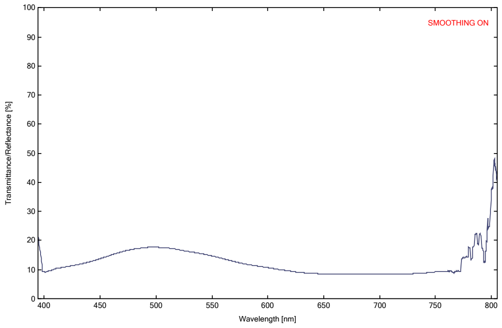


Green earth

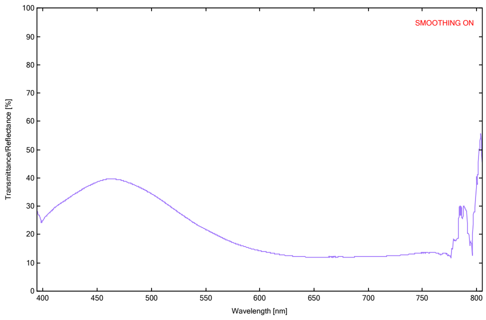
1I

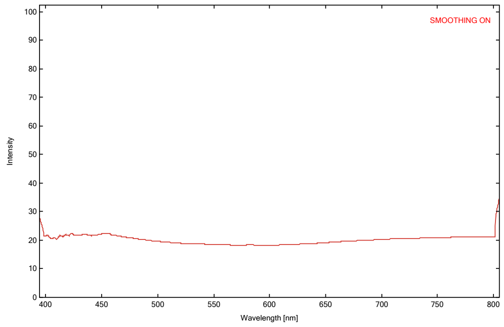


No corresponding reference spectrum.

1J		 Green earth
2A		 Cobalt blue
2B		 Verdigris
2C		 Cadmium green
2D		No corresponding reference spectrum.

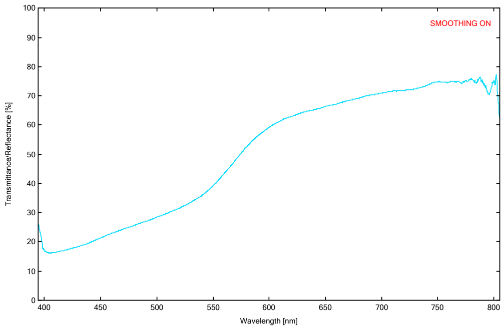
2E

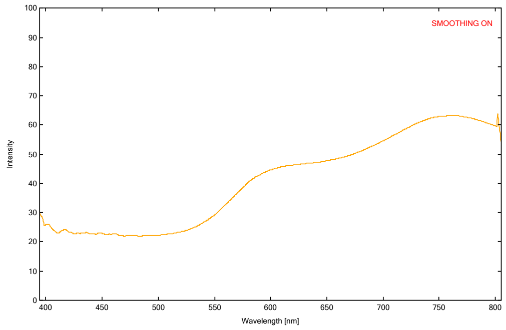




Prussian blue

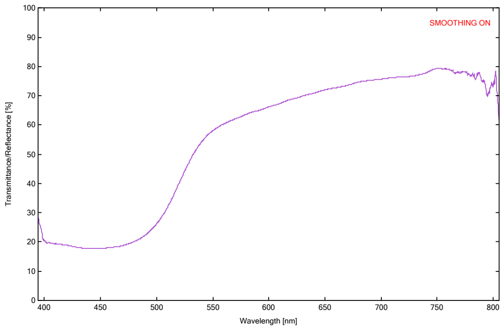
3A

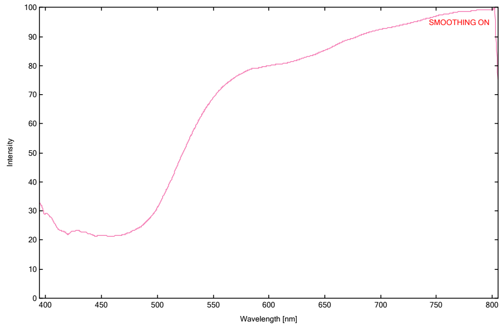




Raw sienna

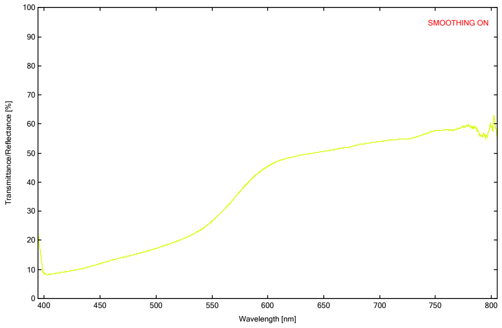
4A

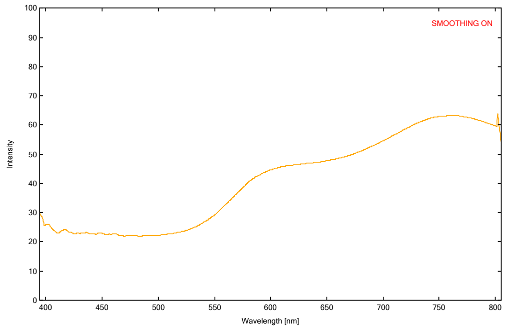




Cobalt yellow

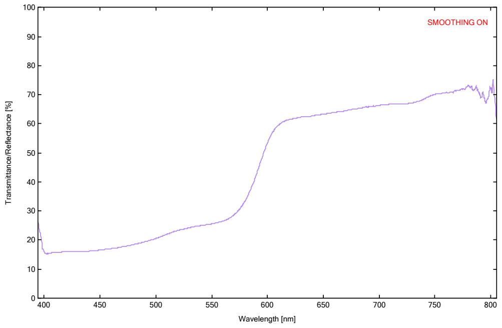
4B

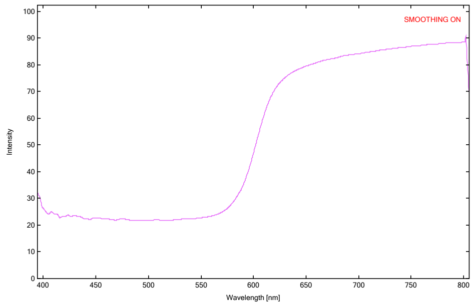




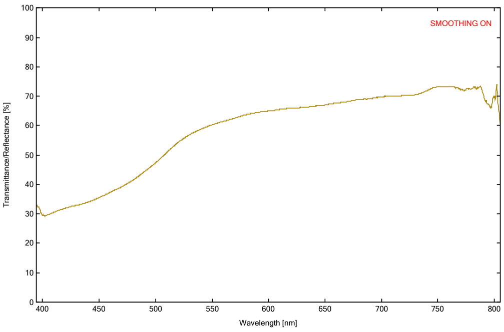
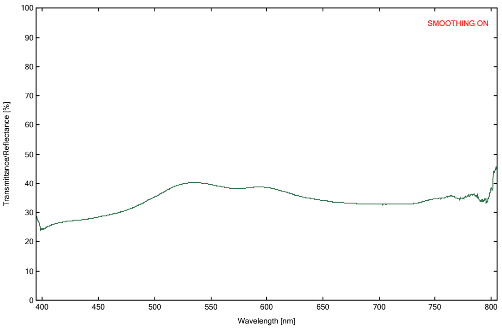
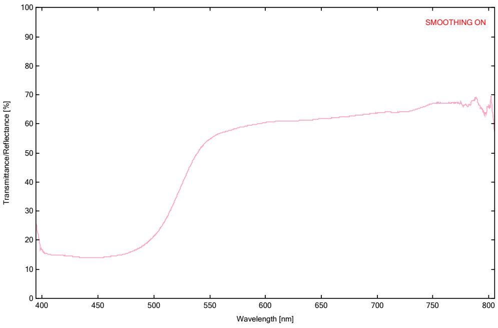
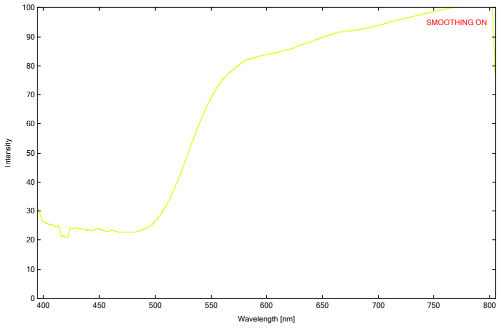
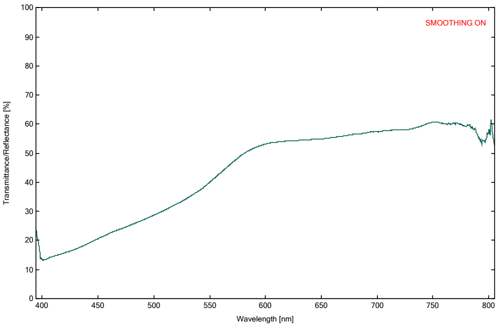
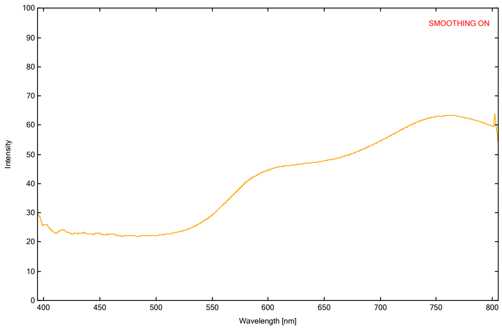
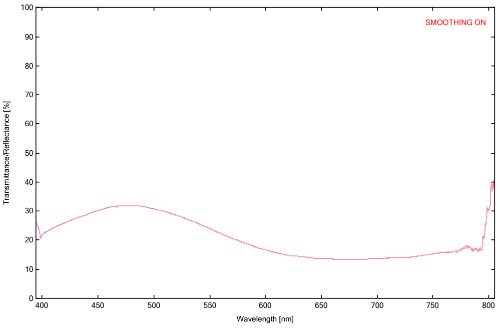
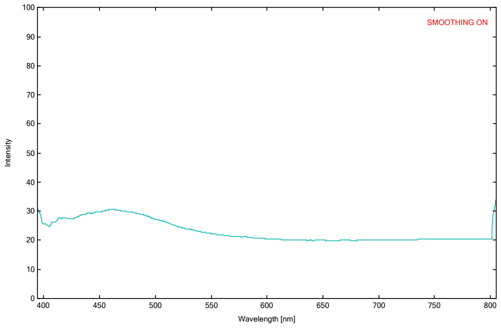
Raw sienna

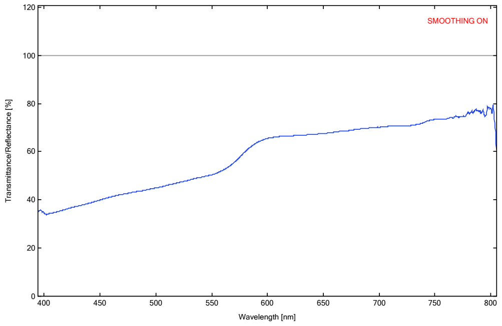
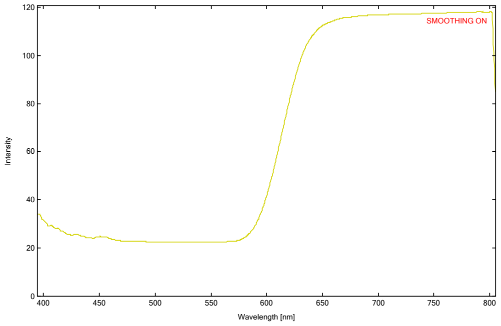
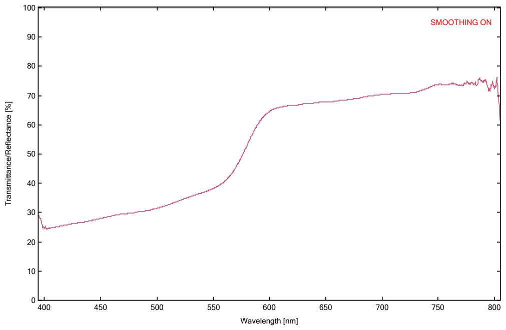
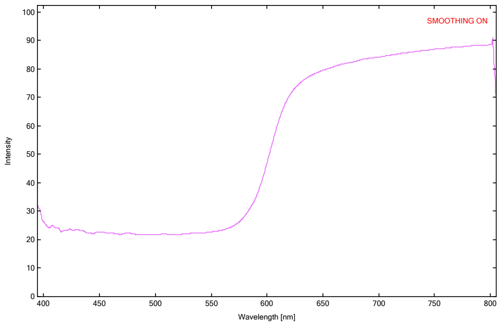
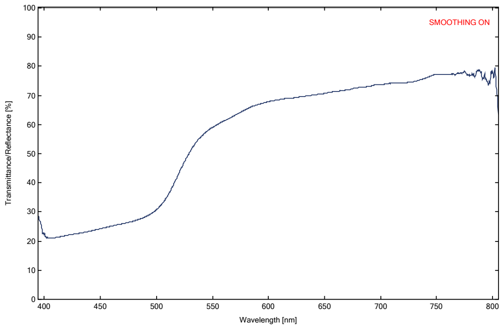
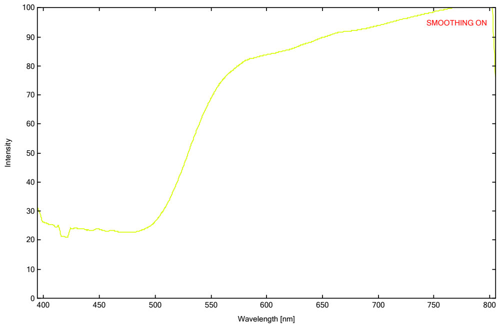
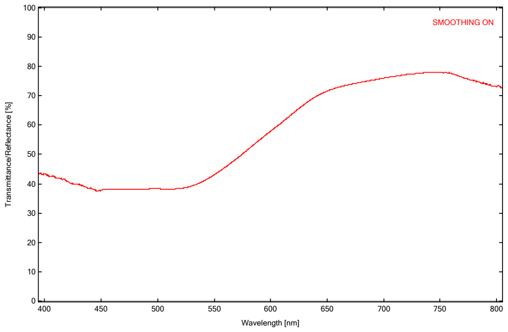
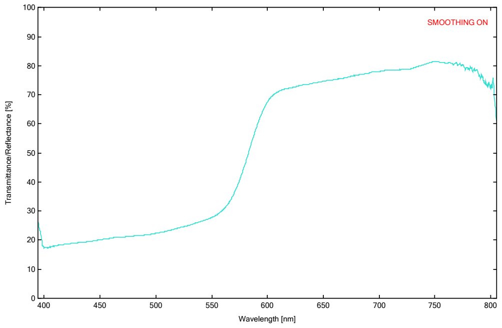
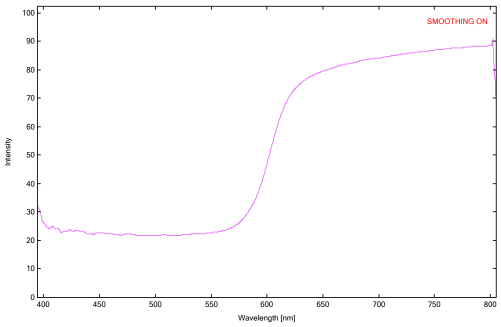
4C

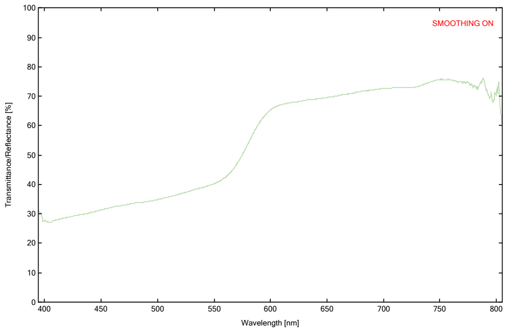
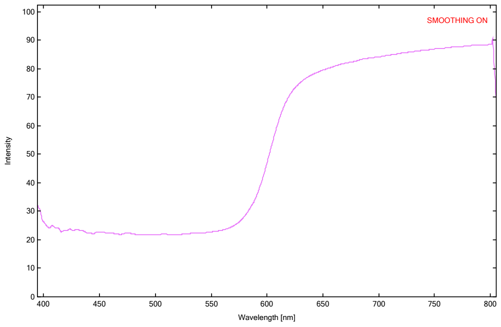
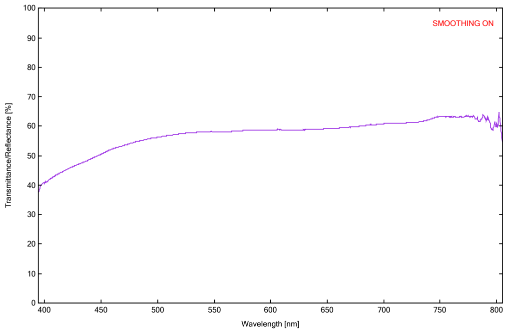




Vermillion

4D		No corresponding reference spectrum.
4E		No corresponding reference spectrum.
4F		 Gamboge
4G		 Raw sienna
5A		 Azurite

6A		 Cadmium red
6B		 Vermillion
6C		 Gamboge
6D		No corresponding reference spectrum.
6E		 Vermillion

6F		 Vermillion
6G		No corresponding reference spectrum.

Appendix 6. XRF Results: Data Reports

Table III. XRF data report results from Bruker Artax-software, of elements detected by XRF in the 31 areas of analysis, of sketch book T 19/2001.

ID	Exposure 1 (40 kv)					Exposure 2 (10 kv)				
1A	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Zn	K12	0,00	758	1	Cr	K12	0,00	166	
	Pb	L1	0,00	38385	160	Pb	L1	0,00		
	Pb	M1	0,00	265	1	Pb	M1	0,00	6392	2
1B	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Cd	K12	0,00	18806	233	Cd	K12	0		
	Cd	L1	0,00		254	Cd	L1	0		1
	Hg	L1	0,00	2913	856	Pb	L1	0		
	Hg	M1	0,00	239	271	Pb	M1	0,00	106784	194
	Pb	L1	0,00	251525	1058					
	Pb	M1	0,00	4279	306					
1C	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Pb	L1	0,00	157359	610	Pb	L1	0		
	Pb	M1	0,00	4117	118	Pb	M1	0,00	93687	211
1D	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Hg	L1	0,00	19647	433	Hg	L1	0		5
	Hg	M1	0,00	511	176	Hg	M1	0,00	12966	231
	Pb	L1	0,00	72830	437	Pb	L1	0,00		
	Pb	M1	0,00	2242	193	Pb	M1	0,00	69407	201
1E	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Hg	L1	0,00	21118	623	Hg	L1	0		1
	Hg	M1	0,00	596	217	Hg	M1	0,00	13620	378
	Pb	L1	0,00	101101	629	Pb	L1	0,00		
	Pb	M1	0,00	2878	227	Pb	M1	0,00	73530	353
1F	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Fe	K12	0,00	4019		Fe	K12	0,00	21714	
	Pb	L1	0,00	9288	5	Pb	L1	0,00		
	Pb	M1	0,00	416		Pb	M1	0,00	8097	
1G	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Hg	L1	0,00	5371	925	Pb	L1	0		
	Hg	M1	0,00	210	414	Pb	M1	0,00	116832	164
	Pb	L1	0,00	280861	1167					
	Pb	M1	0,00	5374	426					
1H	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Fe	K12	0,00	4110		Fe	K12	0,00	21475	
	Zn	K12	0,00	264		Pb	L1	0,00		
	Pb	L1	0,00	14361	24	Pb	M1	0,00	14001	
	Pb	M1	0,00	548						
1I	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Hg	L1	0,00	7732	392	Pb	L1	0		
	Hg	M1	0,00	374	63	Pb	M1	0,00	81152	247
	Pb	L1	0,00	75176	409					
	Pb	M1	0,00	2493	92					
1J	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**	**Element**	**Line**	**Sigma/**	**Net area**	**Backgr.**
	Fe	K12	0,00	1203	1	Fe	K12	0,00	5461	
	Zn	K12	0,00	360	18	Hg	L1	0,00		2
	Hg	L1	0,00	517	11	Hg	M1	0,00	499	52
	Hg	M1	0,00	66	10	Pb	L1	0,00		
	Pb	L1	0,00	3651	5	Pb	M1	0,00	4075	54
	Pb	M1	0,00	104	9					

2A

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	36	
Co	K12	0,00	2535	
Sr	K12	0,00	1593	
Cd	K12	0,00	488	
Cd	L1	0,00		
Pb	L1	0,00	2709	6
Pb	M1	0,00	263	1

Element	Line	Sigma/	Net area	Backgr.
Co	K12	0,00	5683	

2B

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	828	
Cu	K12	0,00	144	
Sr	K12	0,00	1517	35
Hg	L1	0,00	542	16
Hg	M1	0,00	45	
Pb	L1	0,00	6846	30
Pb	M1	0,00	131	

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	4267	
Pb	L1	0,00		
Pb	M1	0,00	12131	46

2C

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	289	
Sr	K12	0,00	1606	8
Cd	K12	0,00	3263	56
Cd	L1	0,00	21	50
Hg	L1	0,00	440	136
Hg	M1	0,00	89	93
Pb	L1	0,00	28186	144
Pb	M1	0,00	991	97

Element	Line	Sigma/	Net area	Backgr.
Pb	L1	0		
Pb	M1	0,00	46579	179

2D

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	1760	3
Co	K12	0,00	884	3
Cu	K12	0,00	205	
Sr	K12	0,00	1490	
Hg	L1	0,00	496	37
Hg	M1	0,00	154	21
Pb	L1	0,00	11636	24
Pb	M1	0,00	390	31

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	4809	
Pb	L1	0,00		
Pb	M1	0,00	23334	72

2E

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	1374	4
Co	K12	0,00	583	5
Sr	K12	0,00	1313	1
Hg	L1	0,00	25	
Hg	M1	0,00	17	
Pb	L1	0,00	348	
Pb	M1	0,00	33	

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	5193	

3A

Element	Line	Sigma/	Net area	Backgr.
Cr	K12	0,00	32	
Fe	K12	0,00	1342	
Pb	L1	0,00	8907	11
Pb	M1	0,00		

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	8825	2

4A

Element	Line	Sigma/	Net area	Backgr.
Cr	K12	0,00	144	
Co	K12	0,00	107	
Hg	L1	0,00	932	370
Hg	M1	0,00	145	39
Pb	L1	0,00	124728	482
Pb	M1	0,00	3495	62

Element	Line	Sigma/	Net area	Backgr.
Pb	L1	0		
Pb	M1	0,00	77879	105

4B

Element	Line	Sigma/	Net area	Backgr.
Ca	K12	0,00	182	
Fe	K12	0,00	2097	1
Hg	L1	0,00	585	80
Hg	M1	0,00	55	2
Pb	L1	0,00	20247	94
Pb	M1	0,00	129	2

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	10934	
Pb	L1	0,00		
Pb	M1	0,00	4503	15

4C

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	34180	436
Hg	M1	0,00	848	25
Pb	L1	0,00	28815	427
Pb	M1	0,00	1150	36

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0		10
Hg	M1	0,00	18319	302
Pb	L1	0,00		
Pb	M1	0,00	32325	284

4D

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	2503	278
Hg	M1	0,00	152	48
Pb	L1	0,00	72049	370
Pb	M1	0,00	1865	71

Element	Line	Sigma/	Net area	Backgr.
Pb	L1	0		
Pb	M1	0,00	62792	170

4E

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	3178	621
Hg	M1	0,00	232	156
Pb	L1	0,00	171446	780
Pb	M1	0,00	4536	179

Element	Line	Sigma/	Net area	Backgr.
Pb	L1	0		
Pb	M1	0,00	107436	201

4F

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	1010	241
Hg	M1	0,00	143	16
Pb	L1	0,00	65653	288
Pb	M1	0,00	1809	31

Element	Line	Sigma/	Net area	Backgr.
Pb	L1	0		
Pb	M1	0,00	51375	87

4G

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	1069	
Cd	K12	0,00	5161	
Cd	L1	0,00	5	
Hg	L1	0,00	577	40
Hg	M1	0,00	83	
Pb	L1	0,00	21202	57
Pb	M1	0,00	34	

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	6539	20
Cu	K12	0,00	449	
Pb	L1	0,00		
Pb	M1	0,00	1858	8

5A

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	340	
Cu	K12	0,00	47	
Zn	K12	0,00	86	1
Cd	K12	0,00	854	
Cd	L1	0,00	16	
Pb	L1	0,00	156	
Pb	M1	0,00	103	

Element	Line	Sigma/	Net area	Backgr.
Fe	K12	0,00	1816	
Pb	L1	0,00		
Pb	M1	0,00	1439	2

6A

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	3001	23
Hg	M1	0,00		1
Pb	L1	0,00	7101	26
Pb	M1	0,00	516	1

Element	Line	Sigma/	Net area	Backgr.
Cd	K12	0		
Cd	L1	0		1
Hg	L1	0,00	14	1
Hg	M1	0,00	5185	177
Pb	L1	0,00		
Pb	M1	0,00	12906	177

6B

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	6936	102
Hg	M1	0,00	220	4
Pb	L1	0,00	10959	106
Pb	M1	0,00	502	5

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	106	5
Hg	M1	0,00	10442	244
Pb	L1	0,00		
Pb	M1	0,00	15939	244

6C

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	653	3
Hg	M1	0,00		
Pb	L1	0,00	4562	4
Pb	M1	0,00	159	

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0		2
Hg	M1	0,00	1459	55
Pb	L1	0,00		
Pb	M1	0,00	15755	53

6D

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	1496	15
Hg	M1	0,00	156	8
Pb	L1	0,00	4420	13
Pb	M1	0,00	139	9

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	78	7
Hg	M1	0,00	2507	243
Pb	L1	0,00		
Pb	M1	0,00	7234	340

6E

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	16799	109
Hg	M1	0,00	669	27
Pb	L1	0,00	4348	96
Pb	M1	0,00	229	31

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	31	25
Hg	M1	0,00	20028	134
Pb	L1	0,00		
Pb	M1	0,00	4841	125

6F

Element	Line	Sigma/	Net area	Backgr.
Cu	K12	0,00	54	
Hg	L1	0,00	3069	18
Hg	M1	0,00	101	2
Pb	L1	0,00	1894	11
Pb	M1	0,00	67	2

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	47	1
Hg	M1	0,00	5715	70
Pb	L1	0,00		
Pb	M1	0,00	2802	92

6G

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	365	1
Hg	M1	0,00		
Pb	L1	0,00	1485	1
Pb	M1	0,00	11	

Element	Line	Sigma/	Net area	Backgr.
Hg	L1	0,00	13	6
Hg	M1	0,00	357	
Pb	L1	0,00		
Pb	M1	0,00	1534	