Use of the ”Video Spectral Comparator 6000” as a non-destructive method for pigment identification

-An experiment

Marthe Aambø

Uppsats för avläggande av filosofie kandidatexamen i Kulturvård, Konservatorprogrammet
15 hp
Institutionen för kulturvård
Göteborgs universitet

2011:5

Naturvetenskapliga fakulteten

GÖTEBORGS UNIVERSITET

Use of the ”Video Spectral Comparator 6000” as a non-destructive method for pigment identification - An experiment

Marthe Aambø

Handledare: Jonny Bjurman

Kandidatuppsats, 15 hp
Konservatorprogrammet
Lå 2010/11

GÖTEBORGS UNIVERSITET
Institutionen för kulturvård

ISSN 1101-3303
ISRN GU/KUV—11/5—SE

UNIVERSITY OF GOTHENBURG
Department of Conservation
P.O. Box 130
SE-405 30 Göteborg, Sweden

www.conservation.gu.se
Tel +46 31 7864700
Fax +46 31 786 47 03

Program in Conservation of Cultural Property
Graduating thesis, BA/Sc, 2011

By: Marthe Aambø
Mentor: Jonny Bjurman

Use of the ”Video Spectral Comparator 6000” as a non-destructive method for pigment identification –An experiment

ABSTRACT
The Video Spectral Comparator 6000 (VSC) is a machine by Foster + Freeman. The machine has many functions in which it uses different light sources to examine documents, and is usually used as a forensic tool to check the validity of valuable documents. The machine is a comparator, and it is often used to compare one set of images or spectra up against another. In this experiment, five functions of the VSC were selected to see if they can be used to identify pigments. These functions were Visual-image, UV-image, Visual spectra, UV-spectra and Spot (fluorescence). First a small reference library was made of 15 Winsor & Newton Artists' Watercolor pigments of the colors blue, brown and green used in the 1920s. The pigments were recorded into the VSC and then six unknown pigments, from five aquarelles by Alexey Zaitzow, were recorded in the same manner. These were then compared with the references. To check the validity of the comparisons, the unknown pigments were also tested with a Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS). Only four of the unknown pigments could be compared properly with the references, since two of the colors were mixtures. Since the comparative material got smaller, additional samples were made by Derwent Studio pencils and Winsor & Newton tube colors. The result of the experiment was that the visual image and the UV-spectra functions were not suitable for pigment identification. The UV-image and Spot (fluorescence) functions might become useful with further tests and an expansion of the reference library. The visual spectra function proved to be most suitable. It could correctly identify most pigments. In the cases were the spectra did not match, this might be because pigment composition was different from what the color name indicated. Therefore this function can probably be used for pigment identification. As background knowledge to the experiment, other non-destructive techniques have been gone through and there is an explanation of light and how it gives the sensation of color.

Title in original language: Use of the ”Video Spectral Comparator 6000” as a non-destructive method for pigment identification –An experiment
Language of text: English
Number of pages: 65 (excluding appendix)
Keywords: VSC 6000, pigment, identification, analysis, experiment, electromagnetic radiation.
ISSN 1101-3303
ISRN GU/KUV—11/5--SE

Acknowledgements

First of all I would like to thank my supervisor Jonny Bjurman for guidance in addition to helping me run the SEM test and understand the results. I would also like to thank the National library of Norway for letting me use the “Video Spectral Comparator 6000”. A special thank you goes out to the conservators there, Nina Hasselberg-Wang, Chiara Palandri and Wlodek Witek, who gave me an invaluable internship as well as the idea for this project.

Next I would like to thank Ida Areklett Garmann, Sarah Fawcett, Anna Stow and Natalie Chalmers for reading and correcting my text. Without you the language and text would be much worse. Lastly my family deserves a big thank you. I could not have done this without my family, who loves me, supports me, and is always there for me no matter what.

Contents

1. Introduction

1.1 Background

As part of my bachelor's degree in paper conservation, I had an internship in the fall of 2010 at the National Library in Oslo, Norway. During my time there I came in contact with the machine "Video Spectral Comparator 6000" (VSC®6000) by Foster + Freeman. From now on this machine will be referred to as the VSC. The VSC is a machine which is normally used by the police to check that passports and other documents are real and not forgeries. The VSC has also had a variety of uses in the cultural heritage sector, like evaluating ink and looking for deterioration in documents. As the name suggests the VSC is a comparator, and works by illuminating a document from different angles and in different light as well as taking spectral measurements. During my time at the library it was suggested to me that it might be interesting to see if one could use the VSC for something it is not specifically designed for, namely to use it to identify pigments. This idea fascinated me and I decided to give it a try.

1.2 Goal

The goal of this project is hopefully to find a new method for use in identifying pigments[1]. The plan is to use five functions of the VSC to first build up a small reference library of known pigments and then compare this library against samples of unknown pigments. This will make use of the VSC as a comparator. To validate the results the unknown pigments will be tested with a Scanning Electron Microscope (SEM), which will give more certain answers of what the unknown pigments are. Then the VSC capability of identifying pigments can be assessed.

An experiment such as this will give insight to one approach of finding out how a specific machine can be used for a different purpose than it was initially intended. If the experiment proves that the VSC cannot be used for pigment identification, the limitations of the machine will be seen and it might be possible to find out what is needed to develop the machine to be used as a method of pigment identification. Another outcome can be that it becomes clear that the approach to the subject was not the right one and that the question needs to be approached from a different angle.

There are many non-destructive analytical instruments on the market today, so it can be asked if another one is really necessary. The results obtained by using the VSC are only indicative and not definite. The reason for this is that the machine is made to compare one set of data to another, and is not an analyzing instrument. But perhaps its results are good enough. Some of the other instruments on the market are expensive to buy and expensive to use, and if a machine is not available at the workplace, analytical services must be bought from an external contractor. This can become very costly. The VSC in itself is a large investment, but the cost of use is not huge. The main item of expenditure is the time and cost of the operator. Other than that it is mainly electricity and maintenance of the machine which decide its cost.

The VSC also has another advantage compared to some of its competitors. It is a machine with more than one function. This can make it a good investment, since one gets a

[1] The word pigment includes inorganic pigments and organic pigments. An organic pigment is a dye which has been precipitated on an insoluble inorganic substrate (lac) (Gettens & Stout 1966, p 120). For the sake of simplicity, indigo, which is used as a dye is here also included under the term pigment.

multifunctional tool, which can perhaps replace other instruments used in a conservation laboratory.

1.3 Issue

The main question to be explored in this experiment is:

- Can the "Video Spectral Comparator 6000" be used as a non-destructive method to identify pigments?

Another question to be briefly examined is:

- What other non-destructive techniques are used today for pigment identification?

1.4 Limitations

Examining if the VSC can be used for pigment identification can be done in different ways. Building a comprehensive reference library of pigments is an exhaustive task and is too big to do properly in a project of this size. Because of the time limit set on this project (10 weeks) tight restrictions have been made.

The pigments chosen for the reference library were mainly those used in watercolors in the 1920s. The choice of using pigments used in watercolors is twofold. One reason is to reduce the number of factors that can influence the results. Watercolor pigments are mixed with gum arabic which is a colorless binder. Therefore it is the pigment itself which stands for the color produced. Painting in other techniques, like oil, the various oils could have different hues, which might influence the color. So by using watercolors the number of interferences that can affect the outcome of the spectra is reduced. In a trial project like this, the fewer factors of interference there are, the better. The other reason for choosing watercolors is the available test-material. The paintings available for testing are all aquarelles. Aquarelle is a watercolor technique, so pigments not used in aquarelles will be superfluous in this experiment.

A further restriction was to the range of colors chosen. Only pigments which are used for blue, green and brown colors were selected. Again the reason for this was to limit the number of colors to be added to the reference library. The choice of these exact colors was because the sketches to be analyzed have mostly these tonalities. The greens are the most uncertain colors, as greens were often mixed from yellow and blue. Still, it is interesting to check whether green pigments were used or if they were mixtures. If they were mixtures it can also be interesting to see if the VSC can distinguish the components.

The VSC has a number of different functions. These functions will be looked closer at in chapter four. In this project only five functions will be used to examine the reference and unknown pigments. Images will be recorded of the pigments in visible flood light and UV-light. Then spectrums will be recorded in visible light, UV-light and in a function called Spot (fluorescence).

1.5 Previous research

There are many different analytical instruments which can be used to identify pigments. Some are destructive and others non-destructive. Some of these instruments can only identify inorganic compounds while others can also analyze organic compounds. Research into these various techniques is extensive, and can be found both in books and articles.

The VSC has been around for some years now, and in different models. Research into use of the VSC is not extensive and certainly does not focus on the area which this thesis covers. If

there is research, is has not been widely published. The focus of use of the VSC has been, for example, to distinguish inks and to detect forgeries. A reason for this could be that the machine has mainly been used as a forensic tool by law institutions. Still the VSC has been used, to some extent, in the cultural heritage sector. Here the use has had a broader application like looking at deterioration, seeing hidden aspects of a document as well as looking at inks and other features of a document. The spread of the VSC in cultural heritage institution does not seem to be extensive yet. A search on the internet revealed that the Smithsonian Institute in Washington has used a VSC to do a colorimetric analysis of postage stamps. The same search showed that The Straus Center for Conservation at the Harvard Art Museum also has a VSC. So by a quick search, it can be seen that the machine is available in some places, but other tools, like Raman Spectroscopy and XRF, are still more dominant (Foster + Freeman, 2011, Harvard Gazette, 2008, Herendeen, 2009, LGC Forensics, 2011, Mokrzycki, 1999).

Research into the subject of using the VSC as an instrument to identify pigments is, as far as I can tell, nonexistent. Therefore this project is a tentative try to do this. The methods of analysis are a selection of the tools that the VSC offers. Others might choose to do the experiment differently. It must be stated that as a conservation student, with limited background knowledge of physics and chemistry, this experiment will be done at a rudimentary level. While other analytical techniques can identify elements or how molecules are combined, and thus use this information to identify pigments, this experiment will only in general look at the shape of the graphs of the unknown pigments and look for similarities with the graphs of known pigments (Appendix 4).

1.6 Method and material

It is the VSC's ability to identify pigments which will be tested in this experiment. As mentioned, five functions of the VSC will be used and evaluated. First a total of 15 selected pigments in the colors blue, brown and green will be recorded with these five functions, and then the six unknown pigments will be recorded in the same way. These unknown pigments come from aquarelles painted by Alexey Zaitzow in 1929. Afterwards the unknown and known pigments will be compared, and maybe indications of which pigments the unknown are can be seen from these comparisons. To identify the actual composition of the unknown pigments, these will be tested with a Scanning Electron Microscope-Energy Dispersive Spectroscope (SEM-EDS). This will then help to validate or invalidate the ability of the VSC to identify pigments. The chapter about the other methods used for pigment identification will be based on literature found in books and articles.

All the figures and tables in this paper are either photographed or drawn by the author. The images of and from the VSC are printed with permission from the National Library, and the photographs of the aquarelles are printed with the permission from Tatjana Zaitzow.

1.7 Literature

To choose the pigments which should be included in the reference library, several sources were consulted. It was as important to exclude pigments as to include them. The main work which was used was "Painting materials: a short encyclopaedia" by Rutherford J. Gettens and George L. Stout. This book goes through all the pigments used up until the 1960's. The book is well renowned and is much used by other researchers. The information found in this book is complemented and verified by a number of other books such as "Artist's Pigments: A Handbook of Their History and Characteristics" edited by Robert L. Feller and "The materials of the artist and their use in painting with notes on techniques of the old masters" by Max Doerner and "Paint and Painting" published by The Tate Gallery.

In chapter two, the section which deals with light and color is mainly based on two books. These are “Light: its interaction with Art and Antiquities” by Thomas B. Brill and “The Science of Paintings” edited by W. Stanley Taft and James W. Mayer. The section on spectroscopy is based on the books “Modern Spectroscopy” by Michel J. Hollas and “Symmetry and Spectroscopy: an Introduction to Vibrational and electronic Spectroscopy” by Daniel C. Harris and Michael D. Bertolucci.

Some of the books listed above are quite old. The encyclopedia by Gettens and Stout was written in the 1960’s and the book by Brill in 1980. It is actually only “Modern Spectroscopy” and “The Science of Paintings” that were written in the year 2000 or later. Still, these other books have merit and give good information. Since the pigments used in this experiment are those used in the late 1920’s, there is no need for information about new pigments on the market. In newer works the works of Gettens and Stout and Doerner are often referred to, which is a sign of their continuous validity. Large parts of the books about light and spectroscopy are also still valid. Some advances in the field have probably happened, but it is only the basics of the theory and methods that are used in this paper. In addition, newer books are also used in these sections, which support and add to the information collected from the older books.

Literature about the various non-destructive analytical methods has been gathered from several sources, which consist of both books and articles in periodicals. The main book used is “Scientific examination for the investigation of paintings: a handbook for conservators-restorers” edited by Daniela Pinna, Monica Galeotti and Rocco Mazzeo. The articles used are too many to mention here, but they come mainly from various periodicals such as “Studies in Conservation”, “X-ray Spectrometry”, and “Journal of Raman Spectroscopy”.

Information about the VSC is mainly based on its manual, since there is not much other material published, and also on my own experience in working with the machine. The experiment itself is as the word says an experiment. The information in the previous chapters is used to understand how the experiment is built up and to interpret the results, along with skills learned throughout the conservation education.

1.8 Disposition

This thesis is built up in the following way: First there is a chapter which reviews what light is and how it gives us color. This chapter is included because all of the analytical techniques used to identify pigments use some sort of electromagnetic radiation to do so. Then the next chapter goes through analytical techniques, on the market today, that are used for pigment identification. This is to give the reader background knowledge to the many techniques that can be used for pigment identification. These methods use different ranges in the electromagnetic spectrum to get identifying characteristics from elements and molecules, and the VSC have functions that is similar to some of these techniques. After that comes a chapter which explains the different functions the VSC can offer. This is to give an understanding of the machine and its versatility. Next is a detailed explanation of how the experiment is conducted. Then the results are listed, and lastly come a discussion of the results and an evaluation of the VSC’s ability to identify pigments. A short list of definitions, and an appendix with pictures and graphs which illustrates some of the deductions made from the experiment, are included at the end of the paper.

2. Light and Color

2.1 What is light?

2.1.1 Light as particles and waves

Light can be described in two ways, as waves and as particles. Both of these ways of describing light are correct and neither of them can explain the phenomenon completely by itself. Light as particles are called photons, which can be imagined as small packets with energy and momentum. Different colors of light are then photons with different energies. The amount of photons per unit area decides its intensity and is often referred to as flux. The energy of a photon is measured in electron volt (eV). One eV is the energy an electron gains when crossing one volt (V). Visible light has an energy range of 1,8 - 3,1 eV. (Brill, 1980, pp 2-7, Hollas, 2004, pp 6-8, Taft et al., 2000, pp 53-55, 106).

Light can also be explained as an electromagnetic wave. The wave has an amplitude *a*. This is the distance from the top of the wave to the average. This is also called the intensity of the wave. The distance between two peaks of the waves determines the wavelength λ. The units for the wavelengths can vary. In this thesis nanometers (nm) will be used. This is a standard and 1 nm is the same as one thousand millionths of a meter (10^{-9}). The wave is in constant motion and the horizontal rate of passage is its velocity *c*, and the frequency *v* is decided by the number of oscillations completed by the wave in one second. Their relationship is described by the formula $c = v \lambda$. Light is an electromagnetic phenomenon, and in electromagnetic waves there is an electric wave and a magnetic wave. It is the electric wave that is the most important when considering light as a constituent of color since it is this wave that affects the electrons and the electric fields in atoms (Brill, 1980, pp 2-7, Harris and Bertolucci, 1978, pp 62-63, Hollas, 2004, p 27).

2.1.2 The electromagnetic spectrum

The electromagnetic spectrum is large, and what we normally think of as light, that is visible light, is only a small part of the spectrum. This is the range roughly between 400-700 nm. Wavelengths with lower energy than visible light are infrared (IR) waves, microwaves and radio waves, while higher energy wavelengths are ultraviolet (UV) waves, x-rays and gamma-rays. The different waves affect atoms and molecules in different ways, which can be seen in the table below (Brill, 1980, pp 7-9). The characteristics of the different wavelengths will be discussed later, first we will see how light interacts with materials to give us color.

Table 1: How various wavelengths can affect molecules. The table is a shortened version from the one found in Thomas B. Brills book: "Light: Its interaction with art and antiquities" (Brill, 1980, pp 8 - 9).

Radiowave	Molecular translations, nuclear reorientations
Microwave	Molecular rotations, electron reorientations
Infrared	Molecular vibrations and direct heat effects
Visible	Low-energy electronic transitions in valence shells
Ultraviolet	High-energy electronic transitions in valence shells
X-ray	Electronic transitions in the inner shells; diffraction by atoms
Gamma-ray	Nuclear transitions

2.2 Light gives color

2.2.1 Light hits matter

Three things can happen when light hits a surface. The light can be absorbed, transmitted or reflected/scattered. When light is absorbed, a photon gives all of its energy to an electron and then disappears. The electron, which gains energy, will, when the incident light is in the visible or UV range, leave its orbital to occupy an empty level further out in the electron configuration around the atom. If the incident radiation has higher energy such as x-rays, the electron will be ejected from the molecule, while lower energy radiation such as IR cannot excite electron and instead causes the molecules to vibrate and rotate.

As an electron leaves its orbital there will be a vacancy which will be filled by another electron from a higher orbital than where the exited one came from. When the electron from the higher orbital makes this transition it will emit a photon. The energy of this photon will be the amount of energy the electron loses in the transition. This energy is the binding energy (E_B) of the first electron subtracted from the binding energy of the electron which fills its place. This value will always be lower than incident photon used to excite the first electron. When the reemission of energy is in the visible region this phenomenon is called fluorescence (Brill, 1980, pp 9, 43-45, Harris and Bertolucci, 1978, p 242, Hollas, 2004, p 122, Taft et al., 2000, pp 75, 81-82, 118-120, 145-149).

Each atom has specific electron energy values, which means that it has characteristic binding energy for the subshells, which gives the atom a unique signature. This can be used for identifying elements. The energy of the incident photons affects what electrons can be excited, and the incident radiation must exceed a specific electrons binding energy to excite it. This is why x-rays can excite electrons in inner shells while visible light can only excite electrons in the valence shells, as electrons in inner shells have higher binding energies. If a molecule is to absorb some of the incident light, this light must have the right amount of energy. If it has the right energy it can heighten the energy state of the molecule, but if the incident radiation's energy is too low or high it will not be absorbed, but instead transmitted or scattered. In general the electron that becomes excited is the one whose binding energy lies closest to the incident radiation's energy. There are other factors besides the incident photon energy which affect absorption. In visible and IR radiation the atomic arrangement and the bonding of atoms decides whether the photons will be absorbed or not. For x-rays, atomic arrangement is not a factor. Instead what is important is the concentration of electrons in a given volume (Brill, 1980, pp 52-54, Harris and Bertolucci, 1978, pp 1-4, Hollas, 2004, p 122, Taft et al., 2000, pp 81-82, 118-120, 145-149).

The second thing that happens to an incident ray is reflection. This happens when the incident light hits a surface of a different medium. The reflected rays will always be at the same angle as the incident rays but on opposite sides to a normal (90º). This follows the law of reflection. Specular reflection is the term used when light is reflected from a smooth and polished surface and diffuse or irregular reflection is when light is reflected from a roughened surface. The first will give the appearance of a shiny surface, while the latter gives the appearance of a matt surface. Diffuse reflection also follows the law of reflection but since the surface is irregular, the rays hit at many different angles, and thus are reflected in corresponding directions. There will be reflection between each boundary the light hits, but the amount is dependent on the difference of refraction between the two substances, a phenomenon which will be explained in the next paragraph. This also determines whether the material is opaque, translucent, or transparent. If the difference in refraction is large, the material will reflect/scatter light effectively and thus seem opaque. Scattering and absorption is also

dependent on particle size and density. Particles around the size of a wavelength and dense materials scatter more effectively than larger or smaller particles, and if the concentration of molecules is high, more light will be absorbed (Brill, 1980, pp 44-46, 61, 95, 99-100, 214, Taft et al., 2000, pp 66-68, 72-73).

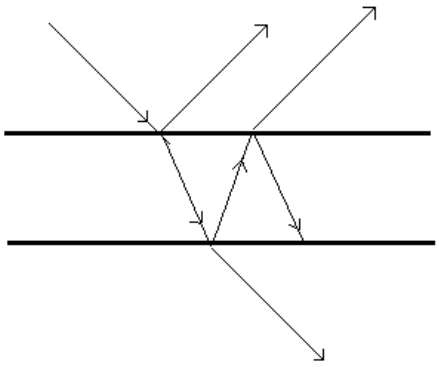

Figure 1: Refraction of light. When light hits a surface it can be reflected, transmitted or absorbed. If it is reflected from the surface, the reflections angle will be the same as the incident light. Transmitted light will be refracted because of the change of velocity. If it goes through the entire object the angle of exit will be the same as the incident light (Taft et al., 2000, p 111)

When light hits a surface it will also be partially transmitted. Once the light goes from one medium to the next, it is refracted. This is because light travels at different speeds in different materials, so when it goes from one medium to another the speed will alter and thus the angle it travels in will also change (Fig 1). The refractive index can be said to be the ratio of the speed of light in a vacuum versus the speed of light in a medium, and the change of the wave's angle can be calculated from the refractive index. If the light goes through the material entirely and comes out in the same medium as it was in before, the angle will equal the angle of incident rays, only shifted slightly (Brill, 1980, pp 44-46, Harris and Bertolucci, 1978, p 66, Taft et al., 2000, pp 66-72)**.**

Materials with a high index of refraction will, as mentioned, reflect more light than those with less, and appear more opaque. Those materials which have high indexes of refraction often have strong absorption as well. This causes little light to escape the material and thus they appear even more opaque. When a light is inside a material, it can be internally reflected. Internal reflection happens when the angle of the wave is greater than the critical angle of incidence and is reflected back into the material. This also is dependent on the index of refraction, and materials with high indexes seem more opaque because less light escapes them than those materials with lesser indexes, and thus critical angle of incidence. So there is a strong correlation between opaqueness and the index of refraction. (Brill, 1980, pp 44-45, 52-55, 95, 99, Taft et al., 2000, pp 66-68).

2.2.2 Color

A materials color is connected to its absorption and reflection of light. White light is composed of wavelengths of all colors in the visible range from red through violet. When light is transmitted in a material, specific wavelengths of it can be absorbed. This selective removal of wavelengths is what causes a color. In principle an object absorbs all wavelengths except the ones which make up their own color. A red surface, for instance, will absorb all wavelengths except the red ones, which will be reflected. This is a spectroscopic pure color, since it has only one wavelength (Fig 2). In reality, however, an illuminated object will reflect a mixture of

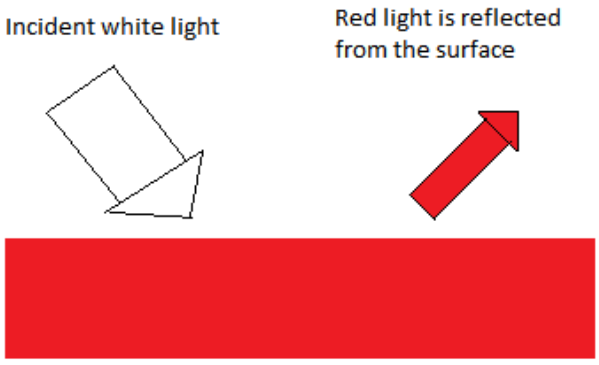

Figure 2: A red object. Incident white light composed of all wavelengths is shone upon a pure red object. Only red light is reflected (Taft et al., 2000, p 62).

wavelengths that are closely spaced around the perceived color, but the specific color will be the dominant wavelength reflected (Brill, 1980, p 59, Taft et al., 2000, pp 51, 55-60, 73-74).

One can use optical instruments to measure the intensities and wavelengths reflected or absorbed, and this can be used to identify pigments. Colors which visually appear the same can be distinguished by such measurement, since their spectral reflectance curve will vary. This means that they absorb different amounts of wavelengths (Taft et al., 2000, pp 55-60).

Different light sources have different spectral composition, and under different viewing conditions similar colors can look different. Incandescent lightbulbs, for example, have stronger emphasis on the longer wavelengths than the shorter, and gives an orange or yellow tinge to the areas it shines upon. Colors that look alike under one type of light, but look different under other lighting conditions are called metameric colors. This phenomenon is among those used with the false color imaging method, and can be used to identify pigments (Brill, 1980, p 20, Buzzegoli and Keller, 2009b, p 200, Taft et al., 2000, pp 60-61).

2.3 The different wavelengths

2.3.1 Infrared (IR) radiation

Infrared radiation has wavelengths from about 700nm-10^5 nm. The wavelengths can be subdivided into categories. The one with the highest energy, which lies next to the red color on the electromagnetic spectrum is called near infrared (NIR), then comes middle infrared (MIR), and lastly far infrared (FIR) (Brill, 1980, pp 12-14, Taft et al., 2000, pp 76-79). IR radiation can in general cause molecular vibrations and heat effects in molecules (Brill, 1980, p 9).

The NIR range can penetrate filters used to block UV radiation and the energies are so low that they are not absorbed or scattered by most pigments. Longer wavelengths of the IR range on the other hand cannot penetrate the same filters. The fact that IR can penetrate further than visible light, has rendered it useful in investigation of artworks. While the upper layers of paint lets the light through, the under-drawings often absorbs it. This effect of infrared radiation has been widely used by museum personnel to see beneath the surface of paintings (Brill, 1980, pp 12-14, Taft et al., 2000, pp 76-79, 125-126, 171).

The MIR range can be absorbed or transmitted by material just like visible light, but instead of electronic transitions it will cause molecular vibrations by bending and stretching the chemical bonds or making the elements in the molecular crystals vibrate relative to each other. Such absorption and transmittance of IR radiation can be recorded by IR spectrometers and used to identify how elements are bonded together (Harris and Bertolucci, 1978, p 93, Taft et al., 2000, p 171).

There are some dangers connected to IR as well. IR causes heating which can affect materials. It can cause drying, shrinking, and cracking as well as speed up other deterioration processes (Brill, 1980, pp 12-14).

2.3.2 Visible light

Visible light lies, as previously mentioned, between 400 nm-700 nm. It is this range the photoreceptors in the human eye can detect. In 1672, Sir Isaac Newton split white light into an array of colors with the help of a prism. This proved that white light is composed of different wavelengths. A wavelength is sensed as a specific color, and the shortest wavelength is interpreted as violet while the longest visible wavelength is perceived as red. Each of the individual wavelengths has a specific color, and by combining all of these, one gets white

light. This is also called additive color mixing. Subtractive color mixing, on the other hand, is what happens when we, for instance, mix pigments. Different pigments will absorb different wavelengths and thus remove these from the light reflected. The spectral distribution of the different colors can be recorded, and used to identify the pigments (Brill, 1980, pp 11, 71-73, Taft et al., 2000, pp 51-53, 55-56, 60-63).

2.3.3 Ultraviolet (UV) radiation

UV radiation lies next to the violet light on the electromagnetic spectrum. It has wavelengths from 10-400 nm. The UV radiation can also be divided further. The 10-180 nm range is called vacuum ultraviolet since it can only be transmitted in a vacuum. Therefore it is not of consequence here. 180-280 nm is the short- or far-ultraviolet, 280-300 nm is the middle-ultraviolet and 300-400 nm is long- or near-ultraviolet (Brill, 1980, p 10, Taft et al., 2000, p 75).

UV is often considered a negative in the conservation world, as it can cause photochemical reactions and bond ruptures, which can be seen in fading and color changes. But UV can also be of use to the conservator in looking at objects. In the art world it can, for example, be used to examine varnish and paint films to see if the image has been retouched. The reason for this is that while visible light is not absorbed by the varnish, the higher energy photons in UV are absorbed, and this can cause fluorescence. Different varnishes fluoresce differently and some modern pigments have different fluorescence than the equivalent traditional ones. UV radiation has also been used to sometimes identify pigments, for example with false color imaging (Brill, 1980, pp 10, 116-117, Buzzegoli and Keller, 2009b, p 200, Taft et al., 2000, p 75).

2.3.4 X-Rays

X-rays are high energy photons with wavelengths in the range of 10 nm-0,03 nm. Paint is relatively transparent to x-rays because of these high energy photons. When absorbed, the x-rays can cause transitions in the inner shells of the atoms and also expel the electron altogether. The amount of absorption depends only on the density of electrons in an area, so atoms with high numbers absorb more x-rays than those with low. But if there is a high concentration of elements of low atomic numbers in a small area, these can also effectively absorb x-rays. The x-rays molecules emit are not dependent on the crystal structure, but instead they are specific to the atoms in the molecules (Taft et al., 2000, pp 79-80, 141).

When an electron is ejected by an x-ray, another electron from a higher orbital will fill its place. When the electron makes this transition it will emit an x-ray. Since each atom has specific electron energy values, the emitted x-rays can be detected and thus the elements identified. The amount of emitted x-rays can also give the amount of the different elements present (Taft et al., 2000, pp 81-82, 145-149).

2.4 Spectroscopy

Spectroscopy is an analytical tool used to evaluate how matter and electromagnetic radiation interact. Atoms and molecules can interact in a set number of ways with the oscillating electric and magnetic fields of light. Spectroscopy primarily looks at the absorption, emission and scattering of the incident radiation by the atoms or molecules. What happens to an atom can happen to a molecule, so for simplicity's sake, this section will only refer to molecules, as most pigments are made of molecules. However it is worth mentioning that atoms do not have rotational or vibrational degrees of freedoms as molecules do. This means an atom can only undergo electronic transitions or ionization, while a molecule can also have rotational and vibrational changes (Harris and Bertolucci, 1978, pp 1, 72, Hollas, 2004, pp 1, 41, 199).

Spectroscopy is done by illuminating a sample with a chosen wavelength or range of wavelengths. The sample can be prepared in different ways and be in gas, liquid or solid phases. The various techniques of spectroscopy have different requirements for sample preparation, but many of them can today be used directly on an area of interest without sampling it. When a sample is illuminated, the spectroscopic techniques measure how much of the incident light is absorbed, emitted or scattered. Measuring absorption can be done over the entire electromagnetic spectrum, while emission is most often measured in the visible or UV-region. An exception is Raman spectroscopy, which will be mentioned in the next chapter. Spectroscopy results in a chart where the absorbed, transmitted, or scattered light is a function of wavelength or wavenumber (Harris and Bertolucci, 1978, p 66, Hollas, 2004, pp 42-43).

In spectroscopy different instruments are used to disperse the incident radiation. The oldest one used is a prism. Prisms have today mostly been replaced by diffraction gratings and interferometers. Diffraction gratings are usually glassy or metallic materials with closely spaced parallel grooves. They can be plane or concave and the material is often coated so it will act as a mirror. An interferometer is harder to explain. J. Michel Hollas (2004) explains it like oil on water with different colors. When white light falls on the water it will be reflected back and forth within the layer and a beam of light emerge from each oscillation. The beams that emerge can interfere with each other either in a destructive or constructive way depending on their wavelengths. It is this interference which gives the colors observed in the oil spill (Hollas, 2004, pp 43, 45, 48).

The detector used in spectroscopy is also important. It must be able to detect the radiation that falls on it. There are different types of detectors to choose from such as photomultipliers and Golay cells, and the choice depends on the spectroscopic method used. Today the charge-coupled device (CCD) is used in many types of spectroscopy. Its normal sensitivity is around 400-1050 nm, but it can be extended to around 1,5 nm (Hollas, 2004, pp 60, 63).

As mentioned above, when an atom or a molecule absorbs energy and the energy state is heightened, the actual reactions depend on the energy of the incident light. Infrared light can excite vibrations in the vibrational energy of the molecule, and is often referred to as "vibrational spectroscopy". Infrared spectroscopy often measures transmitted light, while Raman spectroscopy measure the scattered light (Harris and Bertolucci, 1978, pp 1-2, 93-94).

Visible and UV radiation have more energy than IR. So when an atom absorbs energy from these ranges it can cause a redistribution of electrons within the molecule. This means, as we have seen, that the electron can gain energy and move to an orbital further out. Hence it is the electron's potential energy that is changed and this is called "electronic spectroscopy" (Harris and Bertolucci, 1978, pp 2-3). If the energy is higher the electron can be ejected out of the molecule and cause ionization, a method that is used with spectroscopy which uses x-rays. As infrared changes the rotational as well as vibrational levels, the higher energy radiation also causes vibrational and rotational energy changes. These are, however, obscured by the electronic transition bands (Harris and Bertolucci, 1978, pp 225, 242, 307, 310).

When an excited molecule returns to its ground state, this can happen through two processes. Vibrational energy is lost by nonradiative processes. Its increased energy can be lost by collisions with other molecules, which will heat the entire sample (IR radiation). Electronic energies can be lost by both processes, where the radiative can be in the form of fluorescence, in which light is emitted in the visible range or by first relaxing to an intermediate state by giving off heat and then giving out a photon. A third option, which will only be mentioned here, is chemical reactions (Harris and Bertolucci, 1978, pp 357-360, Hollas, 2004, pp 27-29).

3. Non-destructive analytical methods

This chapter describes non-destructive analytical methods that are used today to identify pigments. The methods will be described briefly on a fundamental level. The goal is to give the reader a basic understanding of what they do and how they work.

While in some literature non-destructive methods are defined as those which do not require sampling, and those which do not damage the sample taken, non-destructive methods will here be defined only as those which do not require sampling (Van Grieken and Janssens, 2005, p 206). Some of the methods in this chapter are normally used as destructive methods, but can in some cases be used non-destructively, and are therefore mentioned here. Some techniques can also do more than just identify pigments on paintings. When this is the case, these applications will be explored as far as the capacity of this paper allows. The list presented here is not exhaustive, but gives a fairly accurate view of what methods are normally used to non-destructively identify pigments.

As described in the previous chapter, the different energies in the electromagnetic spectrum affect the atoms and molecules they hit differently. The lower energy ranges cause vibrations, while the higher energy wavelengths can cause excitation. These features define what information the different spectral techniques give. Those based on x-rays, for example, identify elements, while those based on infrared give information on how the elements are combined. Many of the analytical methods mentioned here, which give different information, can be used in conjunction with each other, and thus become powerful analyzing tools.

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) can analyze both organic and inorganic materials. It is a technique which collects data at single points from the material it analyzes, and identifies molecular groups present in the material. The word “Fourier transform” comes from a mathematical technique which is used to compute the spectrum from the information gained from the instrument (Galeotti et al., 2009, pp 151, 156, Genestar and Pons, 2005, p 270, Martin et al., 2010, p 453, Taft et al., 2000, p 171).

The technique usually requires sampling, but by attaching an external device to it, the method can be done non-destructively, albeit a bit more superficially than with the sampling method. The FTIR can be used as a spectrometer or with a microscope which is called FTIR microscopy. Analysis with FTIR microscopy in the reflection mode is non-destructive (Galeotti et al., 2009, p 154).

FTIR microscopy works by using the ability of the light microscope to see details of a sample and combines it with infrared spectroscopy (IR) which can identify chemical components (Smith, 2003, p 400). The machine illuminates the object with electromagnetic radiation in NIR, MIR, and can also use FIR radiation. As the molecular vibrations of most atoms and molecules are in the infrared region, it is that the FTIR registers. The molecules have specific wavelengths that they absorb, and this is mapped out on a spectrum, where one can see the percentage of absorption or transmission from the IR radiation (Galeotti et al., 2009, p 151).

One problem with the FTIR is that some molecules have overlapping bands of absorption and can thus be hard to distinguish. One method of reducing this problem is by doing a pre-

analysis with a stereomicroscope in order to have an idea of what to expect, and also to compare the result to a reference library of known compounds. If samples from the object are studied, the FTIR can be used to chemically characterize as well as spatially map the organic and inorganic materials on one sample (Galeotti et al., 2009, pp 156) .

The size of the area illuminated is decided by the light sources' size and brightness. In recent years there has been a shift towards using a synchrotron light source combined with FTIR as well as with other spectroscopic techniques, such as X-ray fluorescence (XRF) and X-ray diffraction (XRD). This light source can analyze much smaller areas than what is possible with a normal infrared light source, which is often a thermal source. Synchrotron radiation is made by electrons which are passed through high-field bending magnets. These keep the electrons in an orbit. The electrons then emit radiation from x-rays to the far infrared region (FIR). This causes extremely high brightness, polarization of the light and a very small source size. The synchrotron light source can replace the conventional light source on the microscope, and it also makes the data collection quicker and the spatial resolution higher. The high brightness of the synchrotron light source has not, so far, proved to cause any damage to the material analyzed (Martin et al., 2010, p 453-455, Smith, 2003, p 401-404)

3.2 Fourier Transform Infrared Spectroscopy (FTIR) by fiber optics

This type of FTIR is totally non-invasive and works by adding a mid-infrared fiber optic sampling probe to the FTIR machine. If one has a portable FTIR one can also do analysis *in situ*. The fiber optic probe has 19 chalcogenide glass fibers. Seven of these illuminate the sample in the mid infrared region while the remaining 12 registers the radiation that is reflected from the sample. The area of investigation is about four millimeters wide, which is the width of the probe (Brunetti et al., 2009, pp 157-158).

In comparison with spectrometric methods which measure transmittance, the infrared reflectance spectral data, acquired by FTIR by fiber optics, is more difficult to interpret. The reason for this is that the band patterns and intensities one gets are determined by one or more basic phenomena. This can be diffuse reflection, specular reflection and transflection. In addition there is the drawback that the spectral range is limited to the mid infrared region as well as the fact that absorption bands can overlap, and thus not be easily distinguished. Also to work in the reflectance mode, the spectra can be distorted and thus not comparable to available databases which are based on transmission mode spectrums (Brunetti et al., 2009, pp 157-158).

On the plus side, the lack of sampling makes it possible to take many measurements, and work up statistical data. In spite of the problems mentioned the FTIR by fiber optics is a good method of analysis, and like normal FTIR it can identify both organic and inorganic compounds. If the FTIR is complemented by fiber optics with an non-invasive XRF, the pigments can be identified directly (Brunetti et al., 2009, pp 157-158, Pinna et al., 2009, s 71).

3.3 Fiber Optic Reflectance Spectroscopy (FORS)

FORS is also a reflectance spectroscope which uses fiber optics. But the FORS emits and registers wavelengths in the UV, VIS, and NIR regions. The electromagnetic range possible with some fiber optics used in FORS can be from 250 nm all the way to 11, 000 nm. Only the 2250-2050 cm^{-1} region is a blind spot for this technique. An UV-VIS-NIR reflectance spectrometer normally goes up to the 2500 nm range. By doing so, it can register both electronic and vibrational transitions (Bacci, 2006, pp 47-47, Bacci et al., 2009, p 197-199).

The FORS works by measuring the reflectance diffused from the surface of the sample compared to a reflecting reference standard. FORS has both a spectrophotometer and a spectroanalyzer. The latter is the fibre optic part. It can consist of a probe head with three apertures. Two of these illuminate the sample, while the third one registers the back-scattered light. The angles of the illumination can vary. FORS can be affected by the resthrahlen effect and diffuse and specular light can distort the spectrum. Therefore the optimal angle for each case must be found. Often geometry of 2x45º/0º is optimal. This often makes it possible to avoid the specular reflected light, which does not have any information on the chemical composition. The probe head, and thus the sample size, vary between a few millimeters to a few centimeters (Bacci et al., 2007, p 31, Bacci et al., 2009, pp 197-199, Poli et al., 2009, p 175).

FORS is mainly used to identify pigments, dyes and also to evaluate color and color changes. In comparison to other analytical techniques, FORS is especially apt at identifying dyes. FORS does not require sampling and the instrument is portable. Identification is usually done by comparing the spectra to a database. One of the limitations of the technique is with complex mixtures. In complex mixtures the absorption bands might be shifted or the intensities reduced, which means the result gotten are not very accurate. The yellowing of the binder or varnish in an area of investigation might also shift the curve (Bacci et al., 2009, p 199).

3.4 Imaging Spectroscopy (IS)

IS is a method which is similar to FORS and the techniques can also be used together. Both measure reflected and scattered light as a function of wavelength. IS measures from about 350 nm to 2500 nm, but the wavelengths are divided into three intervals since there is not a sensor that can cover the whole range. As opposed to FORS, information of the whole picture and not only a local point can be obtained, and it is mainly inorganic materials that are identified using IS (Bacci, 2006, p 46, Casini et al., 1999, p 40, Casini et al., 2009, p 165, Pinna et al., 2009, p 68).

Imaging techniques have been used in cultural heritage investigation traditionally to, among other things, look for underdrawings, retouchings and *pentimenti.* One of the techniques used for this has often been near infrared (near-IR) reflectography. With the development of using video cameras instead of analog cameras, and with an increase in the camera sensitivity, the difference in greyness in the pictures taken today can help to identify the pigments used. Imaging spectroscopy is a multi-wavelength imaging system which gives an image and a spectrum (Bacci, 2006, p 47, Casini et al., 1999, pp 39-40, 46).

The IS instruments are portable and can be used *in situ.* The instruments used are spectral cameras. Spectral cameras are digital cameras with narrowband optical filters in front of the lens. The filters are often set on wheels, so the whole spectral range can be used in due course. With this procedure a series of monochromatic images are obtained. These can later on be processed to receive the information wanted. In addition a reflectance spectrum from the instrument is obtained. Together these can identify most pigments (Bacci, 2006, pp 46-47, Casini et al., 2009, pp 165-167, Pinna et al., 2009, pp 68).

Often video cameras are used with IS, but the imaging can also be done with scanning devices. These can either be so called focal-plane or object-plane scanners. The focal plane scanner is in essence a large format camera and is good for in situ measurements. The object-plane scanner is more stationary and the image device moves parallel and close to the surface of the painting (Casini et al., 1999, pp 39-40, Casini et al., 2009, p 166).

One danger of this technique is that it can cause photo-degradation. This is most dangerous with the focal-plane scanner as it illuminates a larger area while the object-plane scanner only illuminates the image zone. This is also the reason why one does not use UV-fluorescence with this instrument. It is mainly the visible and near-infrared region that is used for incident lighting. As with the FORS, it is difficult to get accurate results with complex mixtures, and for the same reasons. In addition, pigments with similar reflectance spectra cannot be distinguished and thus identified. An advantageous side, however, it is possible with the IS to apply computation methods to the images one gets and so get a spatial distribution of the pigments and dyes in the picture, and with hyper-spectral imaging it can also give colorimetric measurements (Bacci, 2006, p 47, Casini et al., 1999, pp 40, 44, Pinna et al., 2009, pp 166-167).

3.5 Optical Microscopy

Optical microscopy is a method that is used to chemically characterize and map, among other things, pigments in a painting in addition to its morphology. White light or polarized light microscopes can be used. The technique usually requires sampling, but if the artwork is small enough to fit on the tray under the lens, it can be used non-destructively (Mazzeo et al., 2009, p 179).

It is with the polarized light one can identify pigments. This method uses two polarizing filters. One is placed before the light reaches the object and the other placed after. The filters have different orientations and when they are crossed, light is extinguished, when they are parallel no extinguishing is shown. During examination, the filters are rotated and the pigments examined will then either become dark four times or stay dark the entire time. If they are dark only at times, the pigments are anisotropic and if they remain dark they are isotropic. These characteristics can indicate possible pigments, but they are just one part of the identification process. One has to explore all the properties that the microscope can offer such as color, morphology, luster, transparency et cetera to identify the pigments. The observations with the optical microscope can be recorded on film or digitally. The technique can also be used in combination with other techniques, such as µRaman and µFTIR to stratigraphically characterize material composition (Mazzeo et al., 2009, pp 179-183).

3.6 Raman and micro-Raman Spectrometry

Raman spectrometry can be used to identify organic, inorganic, crystallized and amorphous materials. The method can be used both destructively and non-destructively. When used non-destructively it can even focus through the glass of a painting, and so the need to disassemble the artwork is removed. In addition one can use portable devices, and so can perform *in situ* work. Since it is a surface analysis method, some problems can come up if the artwork examined has a varnish (Bellot-Gurlet et al., 2006, p 963, Bussotti et al., 1997, p 83, Clark, 2011, pp 13-14, Dran and Pagès-Camagna, 2009, pp 188-189, Pinna et al., 2009, pp 74-75).

In Raman spectrometry it is the scattered light that is measured not the transmitted. A light beam of a specific monochromatic wavelength is radiated on the painting. This light is normally in the visible section of the electromagnetic spectrum, but can also be in the NIR or near-ultraviolet region. The size of the probe head decides how large the spot size will be. The incident light can be absorbed, transmitted or scattered. Part of the scattered light will not change its wavelength. This is what is called Rayleigh scattering. But part of the scattered light will have either a decrease or increase of wavelength, and this is the Raman effect. This scattered light with changed wavelengths is also called Stokes or Anti-Stokes Raman scattering. The vibrational spectrum is specific for molecules. Which pigments can be identified depends on the wavelength of the incident laser beam. This has to do with what

energies the molecules absorb. Therefore more than one incident wavelength must be used to identify all the pigments. Identification of the pigments is done by comparing the spectra to a database of references (Asher, 2002, pp 1-4, Bussotti et al., 1997, p 85, Clark, 2011, pp 13-14, Dran and Pagès-Camagna, 2009, p 188-189, Harris and Bertolucci, 1978, p 94, Hollas, 2004, p 122).

A micro-Raman spectrometer is different from normal Raman in that the sample chamber of the normal Raman is replaced with a microscope. The light is then collected at 180º from the incident light, which is a reversal of the scattering geometry from a normal Raman. This makes it possible to examine a smaller sample or area. A sample can be down to 1 µm. The small size that is possible, and the ability to still get high spatial resolution, makes the micro-Raman method better than all the other techniques that are based on vibrational spectroscopy (Bussotti et al., 1997, pp 85-86).

The Raman technique is easy to use and gives good spatial resolution. It is even possible to spatially map the molecules. The biggest drawback for the technique is that one can often get laser-induced fluorescence. This can make the background too strong and so shade the Raman signals, so the analysis will not be as good. Methods to reduce the risk of fluorescence are being developed, and some show promising results, such as Surface-Enhanced Raman Scattering (Asher, 2002, pp 1-6, Bellot-Gurlet et al., 2006, p 962, Bussotti et al., 1997, p 90, Dran and Pagès-Camagna, 2009, p 189, Hollas, 2004, p 123). Another problem is that the laser excitation used in Raman microscopy can sometimes cause damage to the material analyzed (Martin et al., 2010, p 455).

Raman spectra are usually analyzed visually and then compared with a reference library to identify the materials present. This makes the method subjective and open for interpretation. A method to reduce the margin of error has been made and is today applicable to Raman spectra. This system is called a “fuzzy logic system”. This method is a mathematical formula based on logical calculations. It imitates the reasoning of an experienced observer and in this way either accepts a band in the spectrum as a Raman band or as white noise, and so excludes the latter. One has to choose the width of segment to be used for band detection, and the higher it is the more certain is it that all the bands will be Raman bands, but then with the danger that Raman bands with low intensity will be assumed to be noise and thus excluded. A low segment however can work the other way, and interpret white noise with high intensity as a Raman band. Even with these dangers the fuzzy logic system can be used favorably in interpreting spectra as they exclude subjective conclusions (Perez-Pueyo et al., 2004, pp 808-812).

The Raman technique gives the molecular composition. If one wants the elemental composition of the compounds examined, the technique can be combined with other techniques which detect the elements in the sample. Among others, these techniques can be XRF and particle induced X-ray emission (PIXE) (Bellot-Gurlet et al., 2006, p 963, Bussotti et al., 1997, p 83, Dran and Pagès-Camagna, 2009, 189).

3.7 Ultraviolet/Infrared false color imaging

False color imaging can be used to identify pigments by registering how they look in false color. This technique visualizes what is normally not seen by the naked eye by showing the information one gets from the reflection of UV and IR radiation. Pigments can often be identified using false color imaging, because while colors might look similar in visible light, they may be distinct in UV or IR radiation. Because of the high energy of the UV, it is mainly

the surface pigments that can be recorded, but with use of infrared false color imaging materials under the surface can be reached (Buzzegoli and Keller, 2009b, pp 200, 203).

A picture is made as an RGB image. RGB (red, green, blue) are the colors that are used to make a traditional color image. With false color imaging, one shifts the channels in the RGB images. In false color with UV radiation, the UV image will replace the B component. The blue image takes over the G component and lastly the green image the R component. In infrared the procedure is the same, but instead of eliminating red, one eliminates blue. The IR image will replace the R, red will replace the G and green the B (Buzzegoli and Keller, 2009b, pp 200-201).

False color imaging does not need sampling and is thus non-destructive, but the UV light can cause changes in sensitive pigments and dyes. One cannot always distinguish between pigments with this technique since some pigments look alike in the false colors as well. Concentration and purity and tone can also sometimes affect the colors. Therefore it can be helpful to combine this method with other multi-spectral techniques (Buzzegoli and Keller, 2009b, p 203).

3.8 Ultraviolet fluorescence imaging

UV fluorescence imaging can sometimes be used to identify several pigments, but normally it is used to look at the surface of an artwork. Mostly it is organic materials that fluoresce, and therefore the technique is often used to look at binders, and varnish, but some inorganic pigments also fluoresce. As materials age, the intensity of fluorescence sometimes increases (Buzzegoli and Keller, 2009a, pp 204-205).

The fluorescence in this technique is caused by illuminating the artwork with a mercury vapor lamp. This causes UV fluorescence as well as reflected UV-light. The fluorescence can be captured using a camera with a filter that only allows the fluorescence through, and not the reflected UV-light. Results of the technique can be varied, so to produce constant results one should use standardized procedures. The technique can be used as a preliminary investigation or can also be successfully combined with other methods like false color imaging to identify pigments (Buzzegoli and Keller, 2009a, pp 204-205).

3.9 X-Ray Fluorescence (XRF)

XRF can be used as a destructive and non-destructive method. With mobile instruments it can be used non-destructively as well as *in situ*. The method identifies the elements present and not their chemical state. The method cannot be used to identify organic pigments and dyes. Different factors, such as varnish layers and contaminations, affect the analysis and thus the results are not always only related to the pigment layer in an artwork. The XRF can give information on impurities, which in itself can be useful if the provenance of the artwork is sought after (Dran and Laval, 2009, p 210-213, Hocquet et al., 2008, p 304, 306, Klockenkämper et al., 2000, p 119, Moioli and Seccaroni, 2000, p 48, Van Grieken and Janssens, 2005, pp 1-9, 183-184).

In XRF the object is irradiated with a beam of X-rays or gamma rays from an X-ray tube. Along the beams path, the atoms absorb the radiation and are excited. Then the atoms emit secondary x-rays, which is the fluorescence. If this fluorescence can reach the surface it can be detected. The radiation can be sorted with an energy-dispersive analysis (EDX) or a wavelength-dispersive analysis (WDX) with diffracting Bragg crystals, and analyzed with spectra analysis software. XRF can normally only identify elements from aluminum (Al) to uranium (U). The reason for this is that atoms with a lower atomic number have a low

fluorescence yield, the air can absorb some of the low-energy fluorescence photons, and that their X-ray lines are close and can overlap. With a low size, low power W-anode x-ray tube or a Ca-anode x-ray tube, however, one can come down to smaller elements (Dran and Laval, 2009, pp 211-213, Hocquet et al., 2008, p 304, Klockenkämper et al., 2000, p 122, Moioli and Seccaroni, 2000, p 48, Van Grieken and Janssens, 2005, pp 183-187, 1-9). There are many forms of XRF on the market today. These operate in the same basic manner, but with some modifications. Some of them are: energy dispersive x-ray fluorescence (EDXRF), total reflection XRF (TXRF), microscopic XRF (µ-XRF) and variants of this such as laboratory µ-XRF, portable/in situ µ-XRF, polychromatic synchrotron µ-XRF and confocal µXRF (Van Grieken and Janssens, 2005, pp 267-277).

In addition to analyzing the elements present in an artwork, the XRF can give a quantitative or semi-quantitative measurement. The intensity of the peaks in the spectrum is theoretically proportional to the concentration of the individual pigments but the quantity can be difficult to determine for different reasons. Physical and chemical matrix effects are one problem. This means that factors other than the element itself can cause absorption and enhancement effects. The texture of the analyzed area can, for instance, affect the result as well as impurities present. Today there are ways to correct the matrix effects, which make the quantitative measurement more reliable. In addition, at least one of the new forms of XRF, the TXRF, is not affected by this phenomenon (Dran and Laval, 2009, pp 210-212, Hocquet et al., 2008, p 306, Klockenkämper et al., 2000, p 122-123, Moioli and Seccaroni, 2000, p 48)

Portable XRFs are most useful with other techniques. This could, for example, be X-ray diffraction (XRD). As one identifies the elements and the other the molecules, these could be used together to more easily identify the pigments present. The XRF can also be used as a preliminary analysis to identify the best areas to take samples from and then analyzed with other instruments (Moioli and Seccaroni, 2000, pp 48-49).

3.10 X-Ray Diffraction (XRD)

XRD is a method that is usually used as a sampling technique, but it can be made non-destructive with special set-ups. This makes it possible to do analysis of whole objects, and not just for the sampled area. Organic pigments are amorphous, while inorganic pigments are crystalline particles The XRD can give both qualitative and quantitative results of crystalline materials, but the method cannot analyze amorphous materials (Bomsdorf, 1999, p 2, Castaing and Dran, 2009, pp 207-209).

The technique works by irradiation of the material by monochromatic x-rays. Then the XRD collects photons that are scattered in different angles. The crystals atomic structure is identified by how it diffracts beams of x-rays. The beams direction is determined by the repeated pattern distances. The diffracted beams strength can also vary and is a result of the arrangement of atoms and possible interference with other scattered beams. By comparison with databases, the spectrum can be used to qualitatively and quantitatively identify the compounds present (Bomsdorf, 1999, p 2, Castaing and Dran, 2009, p 207, Taft et al., 2000, pp 135-139, Van Grieken and Janssens, 2005, p 267).

The XRD gives complete identification of the crystalline materials. This means that in contrast to the methods which identify elements, the XRD can tell how these elements are combined. This is especially useful for molecules that have the same chemical composition but different crystal structures. Today it is normal to combine the XRD with XRF to give full material identification. Often these methods are combined in the same instrument. The XRD can also be combined with a particle induced x-ray emission (PIXE) machine. In itself the

XRD has some limitations. As previously mentioned it can only be used on crystalline material, spectral resolution is often low and material with large grains can cause problems. The resolution can today be made better with the use of synchrotron radiation. In contrast to the XRF, where the varnish can cause problems, varnish is transparent to the XRD (Bomsdorf, 1999, p 2, Castaing and Dran, 2009, pp 208-209).

3.11 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS or EDX)

SEM and EDS/EDX are techniques that usually require sampling. If the artwork they are analyzing is small enough to fit in the chamber, it can be done non-destructively, but then the work must also be able to withstand the vacuum created in the chamber along with the bombardment of electrons. To help the situation a low-vacuum SEM can be used. Such variable pressure SEMs (VP-SEM/LP-SEM/ESEM) have gas in the chamber, usually water vapor, that diminishes the charge build-up. Without sampling, the analysis does not yield as much information as with sampling, because with a cross-section one can get information of the sequence and distribution of the pigments in the different paint layers as well (Ineke and Spring, 2009, pp 191-192, Schreiner et al., 2007, s 739).

The SEM can be used on both organic and inorganic materials and is used for both imaging and analyzing. It does this by scanning the surface with a beam of high-energy electrons. The electrons, which interact with the surface, give us information of the surface topography and chemical composition. On an image light elements appear dark, while heavy elements appear light. An analysis gives a spectrum which identifies the different elements present at a point in the sample or object. With SEM only inorganic elements will be distinguishable in a spectrum. The magnification of the test can be as high as 300 000 times and under optimal conditions one can get a resolution down to 1 nm (Ineke and Spring, 2009, pp 191-192, Schreiner et al., 2007, p 740, Van Grieken and Janssens, 2005, p 176).

SEM is often combined with an EDS or EDX. These techniques can register characteristic x-rays emitted from the sample and thus identify elements present in the paint. The EDX can register all elements except hydrogen and helium, while the EDS detect elements from Beryllium and upwards (Barker and Fournelle, 1996, p 1-3, Genestar and Pons, 2005, p 270, Schreiner et al., 2007, p 741). With knowledge about what the chemical composition of different pigments are, the presence of certain elements can indicate which pigments one has, but certain peaks can overlap and make the identification harder. Sometimes an element can be present in more than one pigment, and in these cases the combination with x-ray micro diffraction (XRD), which identify crystalline composition, can help to identify pigments (Ineke and Spring, 2009, pp 191-192, Schreiner et al., 2007, p 741, Van Grieken and Janssens, 2005).

3.12 Particle induced X-ray emission (PIXE)

PIXE is an elemental analysis method. The technique is totally non-destructive and can be used in combination with other methods, such as Raman Spectroscopy. The technique works by bombarding the area under investigation with a beam of highly energetic particles. These particles are often protons and they excite electrons of the inner shells of the elements, which then causes x-ray emission. These x-rays energies are characteristic for each atom, and so the elements present can be detected, but only elements with atomic numbers over 11 (sodium) is usually detectable. In addition to identifying the elements present, PIXE can measure the amount of each atom, which can indicate which compounds are being analyzed. To make the identification more secure, combination with other techniques, such as micro-Raman, can be

beneficial. The technique is fast, and an analysis can be done in 2-3 minutes (Bussotti et al., 1997, pp 86-87).

3.13 Terahertz (THz) spectroscopy

Terahertz spectroscopy is a method that has only recently been developed and used for pigment identification. The terahertz range in the electromagnetic spectrum is between the infrared and the microwave bands. In contrast to x-ray analysis and infrared spectroscopy, which identify organic and inorganic materials, the THz spectroscopy can identify the composites in themselves. Tests done by Kaori Fukunaga et al. (2007) have shown that the method can be used to distinguish pigments, binders and their mixture. The reason for this is that in the terahertz region motions of the whole molecules are dominant. In IR, for example, it is the translational, rotational and vibrational motion in the molecules which are recorded and used to identify pigments. Thus terahertz is more material-specific than techniques which use IR. The equipment used is transportable and analysis can be done fairly quickly (Fukunanga et al., 2007, pp 258-263, Hosako et al., 2010, pp 1-4).

THz spectroscopy can identify most inorganic pigments, as most of these have fingerprint spectra in this region. The technique can also distinguish pigments of the same color and colors in mixtures, if the spectrums of each of the colors in the mixture is known (Fukunanga et al., 2007, p 259). With help from a database of references and a computer program, THz can also give false color images. Such an image can visually show the observer the differences in similar pigments, like natural and artificial ultramarine or different white colors (Fukunanga et al., 2007, pp 260-263). Hosako et al (2010) have shown that the technique can also reveal the depth of cracks and sometimes show the internal structure of artworks (Hosako et al., 2010, p 4).

3.14 Colorimetry

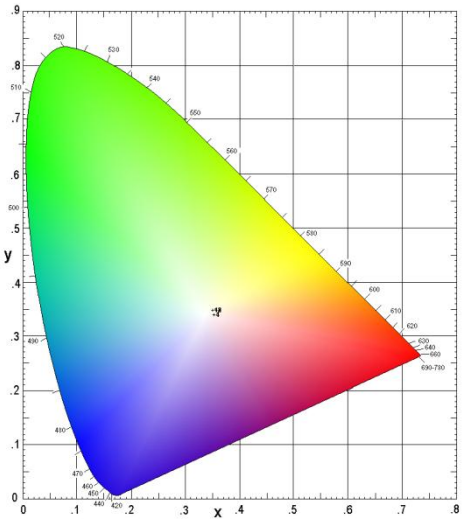

Figure 3: A CIE chromaticity diagram. The dot in the diagram marks the color of the sample.

Colorimetry in itself is a way of quantifying the human color perception. It tries to measure and determine the energy entering the eye and thus give results that are comparable to what is perceived as seen. In conservation it is used, among other things, to see if there are differences in color before and after a conservation treatment, or to monitor fading (Bacci et al., 2009, p 143).

The eye sees colors by three sets of cones. These have sensitivity to red, blue or green. A chromaticity diagram is based on these three primary colors. Three such ideal colors are set at each apex of a triangle. By mixing light of these colors in different quantities one can produce all visible colors. Upon this triangle is laid the *Commission internationale de l'éclairage* (International Commission on Illumination (CIE)) chromaticity curve. Within this curve the different colors actually lie. At a central point in the diagram is white light. This area represents an equal mixture of the primary colors (Taft et al., 2000, pp 65, 128-130).

The Colorimetry method works by giving color coordinates in the color space. This can be done in two different ways. One is to only measure from a determined range of the electromagnetic spectrum. This method gives tristimulus values and chromaticity coordinates

and is used for measuring color. The instrument used for this is a photoelectric colorimeter. The other method uses a spectrophotometer and collects information from the whole visible spectrum. This second method gives a spectrum which shows how much light is reflected or transmitted by the material in the different areas of the electromagnetic spectrum. In addition one gets, as in the first method, tristimulus values. These values can be converted to fit different systems, such as the CIE system. Since the latter method contains more information than the color coordinates this technique can sometimes be used to identify pigments (Bacci et al., 2009, pp 143-145).

A drawback with the spectrophotometer method is that one does not have good resolution and identification of pigments or dyes is limited. Often it is better to use other spectrophotometers that work in a broader range like UV, VIS and NIR. These can often also give colorimetric data (Bacci et al., 2009, p 146).

4. Video Spectral Comparator 6000

The “Video Spectral Comparator 6000” is a PC-based imaging system provided by Foster + Freeman. Foster + Freeman is a company that makes machines used in forensic sciences. The VSC can be used to examine all types of documents and by choosing between various illuminations and viewing conditions, different features can be revealed that are normally not visible to the naked eye. The VSC is mainly built for use in law enforcement and is often used to evaluate if a document has been altered in some way or if it is a forgery (Foster + Freeman, 2011, LGC Forensics, 2011).

This chapter will go through the different features in the VSC to illustrate what the machine can do. In the next chapter the applications used for the experiment will be discussed further. All the information in this chapter comes from VSC manual provided by Foster + Freeman, and a small amount from the official Foster + Freeman web page. Therefore these references will be cited here, but not in the rest of the chapter (Foster + Freeman, 2009, pp 1-95, Foster + Freeman, 2011).

4.1 Set up

The VSC consists of a main unit and a PC-system. The main unit is, as one can see in figure 4 a square box with 3 flaps. In the main unit one has a high resolution CCD firewire color camera with sensitivity from 360 nm to 1100 nm, different light sources, optical filters as well as a translight panel. The panel is situated in the center of the document platen. Underneath the panel are light sources which can illuminate the document from below. The document platen in itself is 650 mm x 650 mm while the translight panel is 235 mm x 175 mm. In the VSC there is also a high resolution grating spectrometer. This can analyze light from a small region in the document. As part of the VSC machinery is a 30” screen and a PC system which is Windows-based.

Figure 4: The VSC main unit is seen on the left and the screen is seen on the right. This picture is of the VSC at the National Library in Norway.

4.2 Settings

The VSC has many settings that can be altered to let the operator get the information he/she wants. The applied settings can be saved as a macro. This enables the operator to recall these settings at a later time if so wanted.

When working with the VSC, one normally works with the live image. This image can be saved on the computer and can be printed. As the VSC is a comparator, a function of the machine is to open a saved document and compare it to the live image via a split screen. Normally the images used are taken by the VSC, but one can also import images taken by an external camera to the VSC for comparisons. Different spectra can also be compared by importing one set of data to another spectrum (Appendix 4, fig 14).

Among the display settings the operator can change is the brightness, specify the sharpness, control the contrast and apply gamma correction in the live image. The gamma correction works by brightening darker areas and thus revealing hidden details. The VSC has auto exposure, which automatically decides the iris and integration time, but the operator can also manually specify the opening of the iris and the length of integration time. Other settings the operator can control are the focus (manual control), magnification (x170) and zoom. The focus also has an automatic button but sometimes this needs a little manual help.

Several tools are available which the operator can use while working. These are, for example, different tools to measure and make annotations in the image. One can, for example, draw a textbox and write in it. Straight or multi-point lines can be drawn, arrows or rectangles/ellipses can be inserted or an area in the image can be defined with a specific color and the rest of the image can be replaced by a white background. A grid can also be applied or crosshairs inserted, to mark the center of the image. The measurement tools available can measure the length between two points, measure a defined area and measure radius and angles defined by three points in the image. The measurements and annotations made can be temporary or they can become a permanent part of the picture. The operator can also choose which color he/she wishes the measurements to be and how opaque they should be.

The VSC has a function which measures the average pixel intensity in two different regions of interest. In addition the VSC can measure variation of illumination in an image. After the measurement this variation can, if wanted, be compensated for. The VSC also offer a function which lets it combine different filters and so determine which ones give the maximum of difference of fluorescence between two areas chosen.

The image toolbar has a variety of effects which can be implemented. One can convert the colors in the image to their complementary colors, reverse the image horizontally or vertically, in addition to rotate the image 90º clockwise or anti clockwise. The image can be made black and white or with the red, green or blue component made to stand out while the rest of the picture is monochrome. A region of interest can be selected either by a rectangular area or by outlining it. This area can be copied to the clipboard. From the clipboard pictures can be imported to other Windows based programs such as Word. When one has two images, these can be made composites in different ways. They can be split horizontally, vertically, strobed, mixed, subtracted and the red and green components can be mixed.

4.3 Light sources and their uses

The VSC has four different light sources. These are used to help bring out specific types of features in the document examined. The first light source is incandescent filament lamps. These have a range from 400 nm-1000 nm and encompass visible and IR light. These lights are used in the VSC when one uses the functions of flood, transmitted, spot and side lighting. The LED lamps which have a wavelength from 400-700 nm are used with coaxial lighting and diffracted lighting. The UV lamps are Vapor discharge tubes. The VSC offers three ranges of UV light. This is with 365 nm (UV-A), 312 nm (UV-B) and 254 (UV-C) peak wavelengths. All of these can illuminate the document from above. With transmitted lighting the VSC only offers UV light with 365 nm. The last of the light sources is a flash tube. This lamp has a range of 850-1100 nm and is used for the Anti-Stokes flash function.

Table 2: Overview over the lamp types, their wavelengths and the functions in the VSC which uses them. The table is recreated from the VSC manual (Foster + Freeman, 2009, p 40).

Lamp type	Wavelength (nm)	Main sources
Incandescent filament lamps	400 – 1000 Visible + IR	Flood lighting
		Transmitted light
		Spot lighting
		Transmitted lighting
		Side lighting
LED	400 – 700 Visible	Coaxial lighting
		Diffracted lighting
Vapour discharge tubes	365 (UV-A)	Transmitted lighting
		Reflected lighting (UV)
	313 (UV-B)	
	254 (UV-C)	
Flash tube	850 – 1100 (IR)	Anti-Stokes flash

The VSC has several functions in which it uses the different light sources from various angles and with filters, some of which can be seen in figure 5. These functions can enhance and reveal different features in a document. Flood lighting uses broad-band illumination for general inspection. It uses two lamps located on each side of the camera. Spot lighting is a more high intensity illumination which only uses one lamp, which is located directly above the document platen. The Spot (fluorescence) function uses narrow-band illumination for excitation. With this function one can choose which filters to use on the spotlamp. It is possible to select shortpass and longpass filters separately to define the wavebands used. When using the Infrared Absorption band-pass filters function, illumination is with a monochromatic light for spectroscopic inspection. Also here one can choose which filters to use and the peak wavelength of illumination.

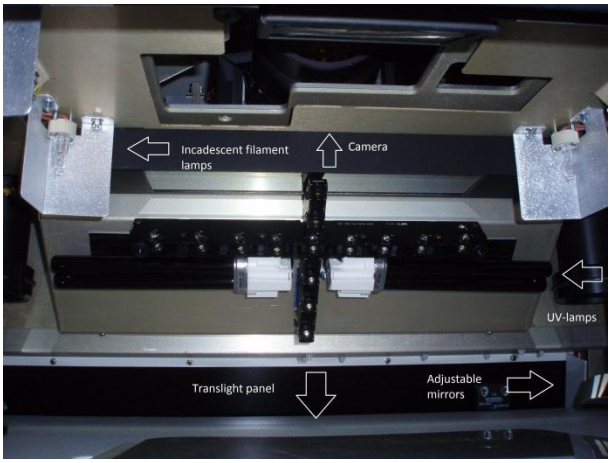

Figure 5: Inside the VSC main unit. The localization of the camera, two light sources, adjustable mirror and the translight panel is marked

With UV radiation one uses monochromatic illumination for excitation for fluorescence measurement, and this work in the same manner as seen in 3.8 Ultraviolet fluorescence imaging. As mentioned earlier for reflected light, it is possible to choose between light with peak wavelengths of 365 nm, 312 nm and 254 nm. The higher energy wavelengths can be dangerous, and the VSC requires all the flaps to be shut tightly before activating the light.

Anti-Stokes flash is a function which uses narrow-band illumination to excite fluorescence. This illumination is in the IR region above 800 nm and lack visible light. When this is done the camera makes an image. One can choose to use a single flash or multi flash in addition to add new exposures on top of each other. This makes it possible to identify, for example, Anti-Stokes security inks which are often used in documents and identity cards. These inks are designed so that they will produce fluorescence in the visible region if they are subjected to infrared radiation.

The VSC offers three different kinds of transmitted light. These light sources are located underneath the translight panel. Here transmitted UV light or transmitted broad band illumination illuminates either the entire panel or a single spot.

Diffracted lighting is a function which illuminates the document from different directions, and is usually used to see Optically Variable Devices (OVD). An OVD is an image made from an electron beam or is a laser generated hologram. The diffracted lighting is a broad-band illumination and one can choose to activate the lights in a specific sequence or individually. There are in total 14 sources located horizontally and vertically and two peripheral sources of light. The OVD viewer controls the diffracted lighting. Here one can choose, among other things, to activate selected light-sources to go in a repeating sequence, and how fast the change from one light source to the next will be (Security Printing, 2007).

The side lighting is also a broad band-illumination. There are two lamps, one on the left hand side and one on the right hand side of the document platen. These can be used separately or they can both be on at the same time. The angle of the side light can be adjusted by adjusting two mirrors in the VSC compartment. The images obtained with side lighting can be mixed in four different ways to reveal different features of the document examined. The minimum pixel value reveals details in dark areas while the maximum gives more detail in bright areas. The average mixing method reduces the contrast in the image and the difference mixing method calculates the pixel difference in bright and dark areas.

Coaxial light is another function the VSC offers. Coaxial light is a light that is shone perpendicularly on the document. Coaxial light reveal retro-reflective features in security documents, which are often used to prevent forgeries. Such retro-reflective features are invisible under normal light but revealed when the incident light is precisely coaxial to the angle of view.

The VSC also has a filter control panel. With this the filters to be used in the camera and the spotlamp while using different functions can be chosen. This can determine if the whole range of the incandescent lamps of 400 nm-1000 nm will be measured, if only the visible light range will be let through the filter, or the operator can choose specific cut-off wavelengths. There is also a function where the VSC applies a sequence of camera filters in turn. This can be used, for instance, to see when a change, like fading, happens in the image. When using certain functions, the VSC can recommend suitable camera filters to be used.

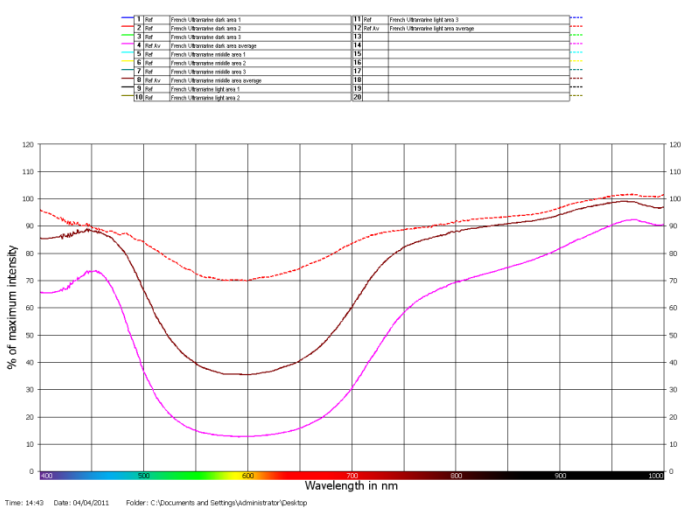

Figure 6: Spectral graphs of French Ultramarine. Here only the averages are shown. Above it one can see which graph has which color

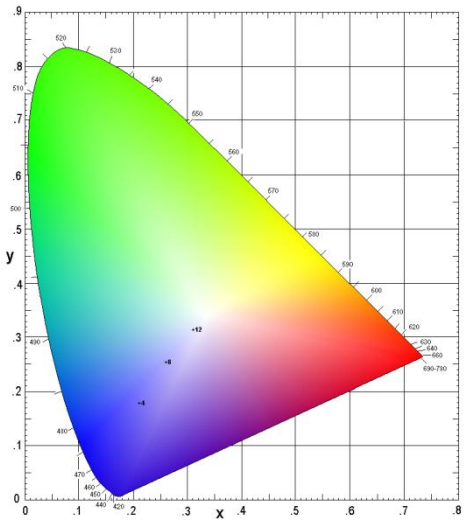

Figure 7: A chromaticity chart of French Ultramarine. The dots show which colors the pigment has in the different measurements. The table with coordinates is not shown

4.4 Spectrum screen

The VSC offers microspectometry with a resolution of up to 9 nm. The spectrum screen (fig 5 and 6) shows a chromaticity chart and a spectral graph after a spectrum has been recorded. In the spectral graphs one can read the plots of light intensity versus the wavelength from 400-1000 nm. At most there can be 20 graphs at one time. There is also a list above the spectrum where one can input textual data of a specific graph and also decide on the color of the different graphs.

There are four types of main spectral graphs. These result from the different methods of measurement used. One can have reflectance, absorption, fluorescence or transmittance graphs. The first two are pre-measured in reference to a standard white tile. The last two do not have a reference signal. Therefore the cameras spectral characteristics and lighting can affect the outcome.

The spectra can be processed in four different ways. The first processing method makes a spectrum that illustrates the difference between two spectra. This function will subtract the corresponding intensity values in the two spectra. One can also normalize two spectra. This will eliminate the background effect so that spectra taken on different substrates can be compared. In this function the spectrum with the least intensity will be altered to match the other spectrum. Another processing method is to calculate the measure of change in intensity with the wavelength. The last processing function is to calculate the average spectra of a number of chosen spectral graphs of the same type (fig 5).

When measuring the spectrum, information in the form of a chromaticity diagram and table is also provided (fig 6). This is based on colorimetric principles as seen in 3.14 Colorimetry. The chromaticity table gives information about the tristimulus values, CIE 1931, CIE UCS 1960 and Colour space 1976, and coordinates are available in one or all of these color spaces. The chromaticity details one gets with a specific VSC is not usable with any other technique or machine. The reason for this is that the narrow-band filter used for spectral analysis with the VSC is wider than the CIE recommends. In addition the color rendering might not be accurate and should therefore only be considered as a guide.

In the same way as the image function of the VSC can have a split screen, which allows the operator to compare and contrast two images, spectra can be opened and inserted with recent or saved graphs. This makes comparison easy and one can easily choose between the graphs wanted at any one time. These comparisons can be saved and printed.

4.5 Size limitations

The VSC can only examine documents up to a certain size. This is because the main unit is a box. Granted the flaps can be opened and thus the document can be larger. But by doing this, the method will not be as reproducible as stray light can affect the examination. Opening the flaps also means that some features cannot be used, such as UVB and UVC radiation.

Foster + Freeman have created another product based on the VSC 6000 which is designed to be used on large formats. It is called the VSC®6000/LF. As this product is built for examination of, among other things, works of art, it is possible that this machine will become more commonly used in the cultural heritage sector than the VSC. It can be designed to suit the materials intended to be examined by regulating the bed size, working distance and magnification range.

5. The Experiment

5.1 Paper

The paper used to paint the pigment references on, is cut from so-called “four flap” envelopes used for photographic storage. The supplier is the company Hans Schröder GMBH. This is a German company which provides materials and equipment for archives, museums and similar institutions (Hans Schröder GmbH, n.d.)

The paper used in the four flap envelope is made of 100% cotton and is acid free, pH neutral and, unbuffered. The paper is naturally white and opaque (Hans Schröder GmbH n.d, Schröder 2010, pp 5, 23). The paper has been tested and has passed the *Photographic Activity Test* (PAT), which is an international standard test (ISO 18916), which was developed by the Image Permanence Institute (IPI) (Hans Schröder GmbH n.d, Image Permanence Institute 2011). There are many papers one can choose to use in experiments such as this. It is because of availability and the qualities mentioned of the paper, that it has been chosen to be used as the support for the reference samples. The envelopes have been cut up, so that one envelope gives five sheets of paper.

5.2 Pigments

The pigments recorded as part of the reference library were carefully selected. The chosen pigments are the ones that are most likely to be found in watercolors from the 1920s. Pigments introduced at a later date and pigments that fell out of use or mostly out of use were not recorded. The reason for this is that the paintings to be analyzed were painted in 1929 and the colors chosen are the ones that are most likely to be found in these pictures.

The pigments used are Winsor & Newton Artists’ Water Colours. The company Winsor & Newton was founded in 1832 in London and strived from the beginning to make the best quality of colors and had a specific focus on permanence. This is the goal the company today still works for (Tate Gallery, 1982, p 8, Winsor & Newton, n.d.-a). Winsor & Newton soon gained popularity all over the world and so there is a small possibility that Zaitzow used colors produced from this company.

The making of colors is in continuous development. Both the pigments used, and the different additions are altered to get the best possible paint. When Winsor & Newton alter their pigment composition, they publish this information. Raw Umber has, for example, been altered lately. Because of this continuous development it is likely that the ingredients in colors produced in the 1920s and today differ to some extent. The binder used in the watercolors is the highest quality of gum arabic, but the binder mix is unique to the pigment, and can be altered. Even if one chose paint from a different company, or made it by hand, there would be a problem of differences in the compositions. Therefore such differences in pigments must be accepted, and hopefully they are not too big so that they will affect the analytical results (Winsor & Newton, 2005, p 2-3, 10-12, Winsor & Newton, n.d.-c).

The colors chosen for the reference library have been restricted to the ranges of blue, green, and brown. Again the paintings have influenced this choice as many of them have these colors, and areas of sampling were easily found. The colors that were recorded can be seen in table 3, along with their chemical composition. The colors alizarin brown and bistre were also planned to be included in the reference library, but these pigments are out of production.

Table 3: The colors chosen to be included in the reference library. (Doerner, 1969, pp 45-95, 259-260, Feller, 1986, pp 141-167, Gettens and Stout, 1966, pp 27-178, Hayes et al., 1979, pp 123-127, Mayer and Smith, 1987, pp 42.91, Merrifield, 1967, pp cxcvi-ccxxv, Roy, 1993, pp 25, 37-67, 113-122, Tate Gallery, 1982, 10-26, Winsor & Newton, n.d.-b)

Pigments used in the reference library	
Blue Colors	
French Ultramarine	Complex sodium aluminum silicate containing sulphur
Prussian blue	Alkali ferriferrocyanide
Indigo	Carbon black, Quinacridone, Copper phthalocyanine
Cobalt blue	Cobalt aluminate
Cerulean blue	Cobalt stannate
Green Colors	
Viridian	Hydrated chromium oxide
Oxide of Chromium	Chromium oxide
Cobalt green	Cobalt nickel titanate
Terre Verte (Green earth)	Natural earth, Hydrated chromium oxide, Cobalt aluminium oxide
Brown colors	
Raw umber	Natural iron oxide
Burnt umber	Natural and synthetic iron oxides
Raw Sienna	Transparent synthetic iron oxides
Burnt Sienna	Transparent synthetic iron oxide
Sepia	Carbon black, Synthetic iron oxide
Vandyke Brown	Carbon black, Synthetic iron oxide

To make the references, a synthetic brush of the type Da Vinci Junior Synthetics Series 303 - Size 4 has been used. To clean it one only needs to use soap and water. The water used was deionized so that a minimum of impurities were introduced to the reference samples. The reference samples were painted in 3x3 cm^2. At the top the pigment concentration is strongest and this is the darkest area of the sample. Down the sample the color becomes lighter and lighter as the pigment concentration is reduced (Great Art, 2011).

5. 3 Functions of the VSC 6000 used to make the reference library

To build up the reference library five different functions of the VSC have been used, using three types of lighting. In visible light overview pictures and spectral measurements have been taken. In UV light, overview pictures have been taken as well as spectral measurements. With the Spot (fluorescence) function, a spot has been used with different filters, to take spectral measurements.

The magnification on all samples has been around 6.20 in the overview pictures, while with spectral measurements, the magnification has been raised to around 15.30. There are some differences in the magnification because of the machine's own recommendations, but the magnifications does not differ more than 0.10 between the samples. Information on the bottom of each picture will tell which magnification that specific picture has along with

information on the time and date the picture was taken, lights used, filters used, auto exposure (integration time and iris), brightness, image width, and if gamma correction has been used.

5.3.1 Visible light

Visible image: From each sample an overview picture was taken. The light used was normal flood light. These images will be used to check if one can tell which pigments are used in paint only by their color.

Visible spectra: The spectral measurements in visible light have been taken in three areas of the sample, where each area has a different pigment concentration. From each of the areas there have also been taken three measurements. The reason for this is that in real watercolors the artist will vary how much pigment is used, and can thus control the color strength. Therefore it can be necessary to have reference measurements with different pigment concentration to increase the possibility of a match with the references. After measuring three times in one area, an average of these graphs has been made. The reason for doing this is that a specific spot might not be representative for the color in that area and thus with three different measurements the chances for getting a representative graph is higher. The spots where the three measurements have been taken lie next to each other. The sheet of paper has just been moved a fraction.

On the computer one can access all the graphs and choose which ones to see, but for the reference album only the graphs of the averages are shown. The reason for this is that with too many graphs at one time it is difficult to read any information.

5.3.2 Ultraviolet radiation

Two wavelengths of UV light have been used to make the reference library. The VSC offers three wavelengths but two was thought to be sufficient to reach the information wanted from the samples. These wavelengths are 365 nm and 312 nm.

UV image: As with visible light, overview pictures of the references have been taken in UV light. These pictures can visually show if the pigments fluoresce in the ultraviolet light.

UV spectra: Spectra are recorded from three different areas of the sample, just as with the visible light. These areas are also from a place with heavy, middle and light pigment concentration. In contrast with the visible light only one spectrum from each spot is taken.

5.3.3 Spot (fluorescence)

Spot (fluorescence) spectra: This function allows images to be illuminated with different wavelengths of visible light, and then fluorescence is recorded in the infrared region. In this experiment three filters were used which represented three ranges of wavelengths which where shone upon the references. The camera adjusts its own filters according to the ones chosen for the incident light, which defines which ranges of wavelengths that will be recorded. The filter choices are listed in the table below.

Certain elements might absorb radiation in one or more of these defined areas of wavelengths and reemit radiation with longer wavelengths close to or in the infrared region. This is why this function is called Spot (fluorescence). This absorption of selected wavelengths might be used to identify pigments. While it is usually objects that is irradiated with UV radiation and which emit visible light, that is called fluorescence, it is the same phenomenon that happens here. This is probably why the function is called Spot (fluorescence), even though one could also call it luminescence. The difference is that the human eye cannot see the emitted infrared

radiation. It can, however, be measured by a spectroscope (Buzzegoli and Keller, 2009a, p 204, Taft et al., 2000, p 75).

As with the UV radiation, measurements have been taken from three areas of different pigment concentration, but only one spot measurement for each area has been recorded. Each of the filters have been used on all the areas of measurement so one ends up with nine graphs in total. With these one can, for instance, choose to look at measurements taken with just the red filter or choose to look at measurements from one area of pigment concentration with one, two or all three of the chosen filters (Appendix 6).

Table 4: The filters used on the spotlight and the camera in the Spot (fluorescence) function.

Filter color	Spot filter transmission graph (in nanometers)	Camera filter transmission graph (in nanometers)
Red filter	645-800	830-
Yellow filter	515-640	695-
Blue filter	400-485	645-

5.4 Selection of aquarelles

The unknown pigments to be tested come from aquarelles painted by Alexey Zaitzow. Alexey Zaitzow was a Russian nobleman who fled to Norway during the revolution in 1918. In Norway he attended Kunstakademiet (Oslo National Academy of the Arts) and graduated from the school in 1926. Zaitzow worked a lot within the theatre where he designed sets and sometimes costumes. The aquarelles used in this experiment are costume sketches which were made for three different plays that were put on for the reopening of Det Nye Teater (The New Theatre) in February of 1929. The plays are from a Knut Hamsun trilogy, and are called "Ved rigets port" (At the Gate of the Kingdom), "Livets Spil" (The Game of Life), and "Aftenrøde" (not translated) (Michelsen, n.d, Oslo Nye Teater A/S, n.d, Stang, 2007).

Five of Alexey Zaitzow's aquarelles were selected to make up the test material. One color was measured from each aquarelle, and two different colors were measured on one of the paintings. The colors chosen were two blues, two browns and two greens. It was attempted to choose colors that looked pure and with little contamination.

The aquarelles are Gammel kvinne (Old wife), En sjømann (A sailor), Bondensen (Bondensen), Musikbandet (The musicband) and Tare (Tare). The latter is the painting where two samples were taken (Appendix 1, fig 1-5).

5.5 Scanning Electron Microscope- Energy Dispersive Spectroscopy (SEM-EDS)

The SEM-analysis was conducted on samples taken from the aquarelles. The samples were taken by scraping of a small amount of pigment with a scalpel and transferring it to a carbon tape. Carbon tape is an inert material and it holds the samples well.

When conducting the test, the samples were first inserted in the SEM, and the distance between samples and the base of the machine was measured. When the SEM was closed, a vacuum was made by extracting out the air. The tests were made by adjusting the distance to the samples, as measured, on the computer. Then one found the area one wanted to analyze and focused the instrument. The area of interest was marked on the computer and the spectra acquired. Then the results were made into Word-files and saved (Appendix 7).

5.6 Sources of error

There are several variables that can influence the result of this experiment. As mentioned, it has been attempted to make the experiment as simple as possible to reduce the number of factors that can influence the outcome. Still there are some factors that one cannot guard against, and these must be taken into consideration when determining if the VSC can be used for pigment identification. Below some of the factors that might make identification difficult are mentioned.

The reproducibility of the experiment is not perfect. As the machine is not an analytical instrument, it is not calibrated as one either. Therefore the results from one VSC might not be the same as results from another. To make the experiment somewhat reproducible, many parameters have been relatively standardized, such as the magnification and substrate, as seen above.

Pigments may change with time. Light can, for example, cause fading, and impurities can affect the colors. While the reference pigments are recorded, on a pure cotton paper, before deterioration processes can affect them, this is not the case with the aquarelles. They are over 80 years old, and might have been exposed to various environmental conditions, which might not be beneficial for their preservation. This can, for example be seen in the paper they are painted on, on which many red spots have formed. Changes to the pigment or the appearance of the pigment with time can cause the measurements taken with the VSC to be different from those of the references, thus making identification more difficult. The validity of the measurements can thus also be questioned. The measured area might not be representative for the pigment for other reasons as well. It might be contaminated, so that one measures the impurities instead of the pigment. The pigment might be altered, by light or pollution, and thus not the same as it was when first applied. Also the substrate might affect the reading, as will be discussed below. To compensate for the possibility of choosing a contaminated area, three measurements have been taken from each of the three areas of pigment concentration when measuring the visible spectrum.

The substrate chosen for the references might affect the outcome of the recorded images and spectra. One way to try to compensate for this has been to take measurements from different areas of pigment concentration. The paper has, presumably, the least influence in the area of high pigment concentration. Unknown pigments that one wants to identify will be on various backgrounds and with varying pigment concentration. Their substrate can also affect the measurements. Since one cannot accommodate for all of the various substrates that can be painted on, this can make pigment identification more difficult. If one later on wishes to expand the reference library, one can reduce this problem somewhat by recording the pigments on more than one substrate, as well as recording the pure pigment powder.

Often pigments are mixed before they are applied to a substrate, or a coating of one pigment can be applied over a coating of another. In paint preparation through history, various additions were added to the paint, and some are still used today. For watercolors some additions has been honey and glycerin (Doerner, 1969, p 257, Tate Gallery, 1982, p 8). The variations of additions and mixtures can be infinite. The reference library only consists of pigments from Winsor and Newton. Later on, one can include other pigment mixtures in the reference library, but one can never include all the possible mixtures. While analytical techniques which identify elements can usually find which pigments have been mixed, this might not be done in a high degree with the VSC. This can be a drawback with this method of pigment identification.

All of the conclusions drawn in this paper are subjective and done by one person. Comparing images and graphs leaves room for interpretation and others might have differing opinions. If such comparisons are to be more objective, several qualified people need to have examined the results and agree on them. But even this might not give results that are objective enough. One of the reasons is because of the amount of data one needs to process. In this experiment only a selected list of reference pigments has been chosen, but still it is much information. The more material there is to compare, the easier it is to make mistakes. An option to solve this is to create a database which can mathematically calculate matches. This will remove the subjective opinions and general human errors.

In this experiment the VSC is thought of as a non-destructive technique. This is only half-true as some of its functions can be destructive. UV is known to have degrading effects on pigments. The longer the exposure the higher is the risk of deterioration. This is important to keep in mind when using the UV-functions in the VSC. Visible light in general can also cause damages, but it takes longer exposures than with UV. With the flaps of the VSC down, which is recommended to get as accurate results as possible, the temperature of the chamber will rise, as a result of infrared radiation. The longer the work session, the higher the temperature will get. This heat can also cause damage to the documents examined. Therefore the operator should try to limit both the use of UV-light and the length of investigation.

To validate or invalidate the results of the comparisons, SEM will be used to identify the unknown pigments. One problem is that the SEM can only identify inorganic pigments. If some of the unknown pigments prove to be organic, it will only be able to tell that they are organic and not their elements. As the SEM was the only analytical machine available to be used in this project, this can be a potential problem.

6. Results

In this chapter the results from the experiment are documented. The results are subjectively drawn and come from a visual examination in which the reference pigments have been compared to the unknown pigments in the aquarelles. In this chapter and the next, the unknown pigments will be referred to as samples, while the known pigments are referred to as references.

6.1 Results from the VSC 6000

6.1.1 Old wife

Visual image: The color of the dress of the "Old wife" is very dark, and has almost a blackish tone in some places. The references that looks most like this color is the darkest areas of Indigo and Prussian Blue (Appendix 1, fig 1. Appendix 2, fig 6 and 7).

UV-image: The UV-pictures show no visible fluorescence. None of the blue references has fluorescence either, except Indigo, which show some fluorescence in its lighter areas with UV 312 (Appendix 3, fig 11).

Visible spectra: The graphs from "Old wife" have low intensity, and they have small peaks around 450nm. They then take a dip and are at their lowest around 575nm and then start rising again and flatten out somewhat after 750 nm. The ending point is with a slightly higher intensity than the start point (Appendix 4, fig 13).

The spectrum which looks most like the samples is from French Ultramarine. These graphs change in the same areas, but vary more strongly in intensity. It is the graph taken from the light area of the reference which is most similar in form, but at the same time it is dissimilar in intensity (Appendix 4, fig 13).

There are some similarities with the graphs of Prussian Blue as well. But in all these graphs there is a small peak at around 660 nm which the sample lacks. Even though the graphs of Prussian Blue and the sample are similar in form, they are not as in phase as the sample is with the French Ultramarine.

UV-spectra: It is hard to tell which graphs look most like the UV-graphs taken on the sample. Many samples and references can have some of the same characteristics in one wavelength, but at the same time look different with different wavelengths. The French Ultramarine and Prussian Blue have a few similarities. The most similar is Cerulean Blue in 365nm. Therefore this comparison can be regarded as inconclusive.

Spot (fluorescence): The graph of "Old wife" recorded with the red filter has some similarities with the measurements from almost all the references. In general, the blue references recorded with the red filter, are very similar. And these all have their main peaks in the same area as the "Old wife". Prussian Blue is the only pigment that stands out by not having similar graphs.

The blue filter spectrum can look like many of the blue references measurements from areas of light pigment concentration, but Cerulean Blue has the strongest resemblance. As will be explained more in the next chapter, the graphs recorded in the light area of pigment concentration, often look like the measurements taken from plain paper. In these areas, the paper might shine through and affect the results. Therefore in the comparisons from here on, the main focus will be on the areas of middle and dark pigment concentrations, in both the

references and the samples. Comparing the samples graph measured with the blue filter, the references from middle and heavy areas of pigment concentration resemble the ones of Indigo and French Ultramarine.

The spectrum recorded with the yellow filter does not bear close resemblance to any of the reference graphs. One of the graphs from both French Ultramarine and Indigo has the main peak in the same area, but the shapes of these graphs do not fit the sample's graph (Appendix 6, fig 31, 33-35).

6.1.2 A Sailor

Visible image: Which of the references colors "A sailor" looks most like is hard to determine. French Ultramarine or Cerulean Blue is a possibility, but none of the references are identical with the sample (Appendix 1, fig 2. Appendix 2, fig 8).

UV image: The UV images from "A sailor" show no fluorescence. This only eliminates Indigo as a possibility.

Visible spectra: The visible spectra of "A sailor" look quite similar to French Ultramarine. They also look like the spectra of "Old wife", only with larger fluctuations (Appendix 4, fig 14).

UV-spectra: The spectrum taken with UV 365 looks a little like the Cerulean Blue, French Ultramarine, and like Indigo. UV 312 looks like Cerulean Blue and Prussian Blue (Appendix 5, fig 27-30).

Spot (fluorescence): The spectra recorded from "A sailor" have two peaks. One is around 740nm and the other around 775 nm. Cerulean Blue and French Ultramarine have the most similar red peaks.

The recorded graph, taken with a yellow filter and in the light area of pigment concentration of "A sailor", looks similar to the corresponding graph of "Old wife". The graph recorded in the area of middle pigment concentration is similar in intensity to the first graph but is shifted slightly to the right. In addition the second graph is not as smooth as the first. The spectrum from the area of middle pigment concentration looks a little bit like Indigo or Cerulean Blue. The spectrum recorded from the area with heaviest pigment concentration, have some similarities with the middle area graph, but here again the intensity has shifted slightly to the right. This last graph might bear the most resemblance to Indigo, but only in that its peak is located in the same area.

The spectra of "A sailor" recorded in the area of light pigment concentration and taken with a blue filter, looks like French Ultramarine, Cerulean Blue, Cobalt Blue and Indigo. The most alike are the spectra recorded in the light areas of these references. The middle and dark area spectra of "A sailor" look a little like each other with a peak at around 660 nm, and then a flatter area with smaller peaks. However, the area of heavy pigment concentration has a larger peak again at around 770 nm which the graph from the area of middle pigment concentration lacks. The only sample that bears a little bit of resemblance to this is French Ultramarine (Appendix 6, fig 32-35).

6.1.3 Bondensen

Visible image: the brown color on the frock in the image "Bondensen" is quite dark brown. From the images it bears most resemblance to Burnt Umber (Appendix 1, fig 3, Appendix 2, fig 9).

UV-image: The UV-images show no visible fluorescence of the brown color in any of the ultraviolet wavelengths. None of the reference samples in UV-light showed any fluorescence either, so comparison here could not exclude any of the references.

Visible Spectrum: The visible spectral graphs have a gradual continuous rise which peaks at around 950 nm. Comparing these graphs to the reference spectra they look most like the graphs from Burnt Umber and second most resemblance to Raw Umber and Sepia (Appendix 4, fig 15).

UV-Spectra: The graphs taken with UV 365 had high intensity in all areas of pigment concentration. The graphs had top peaks around 540 nm. Only the graphs from the light areas of pigment concentration recorded from Raw Sienna and Raw Umber and Sepia show similar spectral distribution and intensities. The graph taken from the area of the sample with high pigment concentration looks somewhat like the graph in Raw Sienna taken from an area of high pigment concentration, and a graph measured from an area of light pigment concentration in Vandyke Brown. Other than that it is hard to draw any conclusions.

With UV 312 the graphs that look most like the samples are from the areas of light pigment concentration in Burnt Umber and Raw Sienna. The intensities of the graphs here are less than with 365 nm, but still high compared to the references.

Spot (fluorescence): First it should be mentioned that with the "Bondensen" image, the measurements taken from different places, but with the same filter, yield almost identical graphs in both form and intensity with the blue and yellow filters. The red filters also yield similar results, but these are not as identical as the two others.

The spectra taken with the red filter does not really look like any of the references graphs recorded with a red filter. The closest one gets might be Burnt or Raw Sienna.

When looking at the yellow graphs, it is the areas of light pigment concentration from Raw Sienna, Burnt Umber or Burnt Sienna that look most like the samples. Since these also look like the papers graph and I have decided to disregard them, the closest graphs are Burnt or Raw Sienna and Sepia, but these graphs have extra peaks which the sample does not have.

For the blue spectra, the trend is the same with the light areas of pigment concentration matching best. Ignoring those, Raw Sienna or the Umbers have the most similar graphs, but they do not look much alike (Appendix 6, fig 36- 38-42).

6.1.4 The musicband

Visible image: The color of "The musicband" is very dark brown with a red tone in it. It is so dark that in some places it looks black. When comparing the color with the brown references, it does not look identical to any of them, but Burnt Umber comes closest (Appendix 1, fig 4, Appendix 2, fig 9).

UV-image: The brown of the sample does not fluoresce and neither do any of the references.

Visible spectrum: The graphs taken with visible light all start roughly in the same area and their intensities rise gradually up until 960 nm. The area with the heaviest pigment concentration has the least increase in intensity, while the areas of middle and light pigment concentration have correspondingly higher increases in intensity. The graphs show strong similarities with two pigments. These are Burnt Umber and Sepia. The graph with the lowest intensity looks most like Sepia, while those with higher intensity, look more like Burnt Umber (Appendix 4, fig 16).

UV-spectra: The UV-fluorescence measured from the sample is very low, and there is little difference in intensity between the different areas measured. It is difficult to compare these spectra with the references, but the one that might have the most similar features is Burnt Umber. Other references which might have some similarities are Sepia, Vandyke Brown, and Raw Sienna.

Spot (fluorescence): The graphs taken with the red filter do not have a high degree of similarity with any of the references, but they might look a little like Burnt Umber or Sepia.

All of the graphs from "The musicband" have their main peak around 710 nm when using the yellow filter. Also here it is difficult to say which references bears the closest resemblance, as none of them have a strong likeness. All the Siennas and Umbers can have some similarities.

The blue filter spectra bear resemblance to Raw Sienna, Raw Umber and Burnt Umber (Appendix 6, fig 37-42).

6.1.5 Tare 1 (light green)

Visible image: This light green is a quite clear green color, but it does not seem to have as much hiding power as the darker green (Tare 2). From the reference images, it looks most like Oxide of Chromium (Appendix 1, fig 5. Appendix 2, fig 19).

UV-image: The UV-image shows that the green has no visible fluorescence. None of the reference samples has visible fluorescence either.

Visible spectrum: The graphs, taken with visible light, have a sharp rise from around 440 nm and reach a peak at around 525 nm. They then fall again until 675 nm where they rise again. These graphs do not look much like any of the references (Appendix 4, fig 17).

UV-spectra: It is hard to compare the UV spectra. The one taken with wavelength of 365nm has many similarities with all of the references except Viridian. The spectrum taken with the wavelength of 312nm might look like Cobalt Green but again the resemblance is not striking.

Spot (fluorescence) spectra: All the reference's graphs taken with the red filter has peaks in the same area as the sample, but none of them have intensities that match the sample.

The graph recorded with the yellow filter does not match the references well, but Terre Verte and Cobalt Green come closest. The graphs of the references taken in the area of light pigment concentration match the sample most, so there is a possibility that the paper shines through and affects the graphs recorded from "Tare 1".

None of the reference graphs taken with the blue filter matches the sample well either, but again Terre Verte and Viridian come closest. As before measurements taken from the areas of light pigment concentration have the closest resemblance (Appendix 6, fig 43- 45-47).

6.1.6 Tare 2 (dark green)

Visible image: As with the lighter green color, this darker green bears most resemblance to the pigment Oxide of Chromium (Appendix 1, fig 5. Appendix 2, fig 10).

UV-image: The dark green color does not have any visible fluorescence and none of the references have fluorescence either.

Visible spectra: The graphs of the dark green color are quite flat. There is a slight rise from the beginning until 525 nm then they decline until around 675 nm and then they rise again. When comparing the light and the dark green spectral graphs they look very similar, but the

darker color's graphs have less intensity and they are a flatter version of the light green colors graphs. As with the light green, they do not bear any strong resemblance to the other reference graphs (Appendix 4, fig 18).

UV-spectra: As with the light green color the UV spectrum with the wavelength of 365 nm have similarities and differences with most of the reference spectra, except Viridian. With UV 312 nm it looks most like Terre Verte.

Spot (fluorescence): The sample's graph taken with the red filter has its main peak around 775 nm. The reference resembles most is Viridian (Appendix 6, fig 44-47).

The yellow spot looks most like Cobalt Green and Terre Verte. As with the light green the reference graphs taken from areas of light pigment concentration have the best match.

The graph taken with the blue filter has similarities and differences with most of the green references. Which one comes closest is hard to determine, so none will be chosen here.

Table 5: Overview of the results from the visual comparison of the unknown pigments with the reference library. The results with question marks are uncertain results.

Results from the VSC comparisons					
Sample	**Visible image**	**UV-image**	**Visible spectrum**	**UV-spectra**	**Spot (fluorescence)**
Old wife	Indigo, Prussian Blue	Undetermined	French Ultramarine	Cerulean Blue, French Ultramarine, Prussian Blue (?)	All except Prussian Blue (?)
A sailor	French Ultramarine, Cerulean Blue	Undetermined	French Ultramarine	Can look like all of the references (?)	All except Cobalt Blue (?)
Bondensen	Burnt Umber	Undetermined	Burnt Umber, Raw Umber, Sepia	All except Burnt Sienna (?)	All except Vandyke Brown (?)
The musicband	Burnt Umber (?)	Undetermined	Burnt Umber, Sepia	Burnt Umber, Raw Sienna, Sepia, Vandyke Brown (?)	All except Vandyke Brown (?)
Tare 1 (light green)	Oxide of Chromium	Undetermined	None	All except Viridian (?)	Cobalt Green, Terre Verte Viridian (?)
Tare 2 (dark green)	Oxide of Chromium	Undetermined	None	All except Viridian (?)	Cobalt Green. Terre Verte, Viridan (?)

6.2 SEM results

6.2.1 Old wife

The SEM showed that this sample contained aluminum (Al), sodium (Na) and sulphur (S). These elements are all present in Ultramarine. So most likely the pigment that is used here is (French) Ultramarine (Appendix 7, fig 48).

6.2.2 A Sailor

As in "Old wife", this sample contains Al, Na and S. So this pigment is also (French) Ultramarine (Appendix 7, fig 49).

6.2.3 Bondensen

The elements present in this sample suggest that it is an earth color. The large amount of iron (Fe) present can indicate that the pigment is Umber or Sienna which both are iron oxides. Some Manganese (Mn) was also present, which can indicate that the earth had manganese in it.

6.2.4 The musicband

As in "Bondensen" this sample is also probably an earth color, and most likely an Umber or a Sienna. The dark color of the pigment can suggest that it is Umber.

6.2.5 Tare 1 (light green)

There is a large amount of lead (Pb) and chromium (Cr) present in the sample. This indicates Chrome Yellow. Since the color is green it is also likely to be mixed with a blue color. The large amount of iron present can indicate that the blue color is Prussian Blue. This was a normal mixture which is called Chrome green (Gettens and Stout, 1966, p 105).

6.2.6 Tare 2 (dark green)

As in "Tare 1" this sample also contains Pb and Cr which indicate Chrome Yellow. The blue mixed in can be Prussian Blue and/or Ultramarine, as the elements for both are present.

Table 6: Overview of the results from the SEM-analysis.

Sample	**Pigment**
Old wife	French Ultramarine
A sailor	French Ultramarine
Bondensen	An earth pigment
The musicband	An earth pigment (maybe an Umber)
Tare 1 (light green)	Prussian Blue and Chrome Yellow
Tare 2 (dark green)	Prussian Blue and/or Ultramaine and Chrome Yellow

7. Discussion

From chapter six it can be seen that the five methods of measurement tested in this experiment did not yield identical results in identifying which pigment an unknown sample could be made of. Where the sample looked like one pigment in, for example, the visible image, the same sample might look most like another pigment in the visible spectra. Which of the techniques tested here is most likely to be correct will be discussed in this chapter, and the SEM results will act as a guide to this assessment.

Only the two blue samples could be given a firm identification with the SEM, and due to the fact that they turned out to be the same pigment, this was considered to be insufficient comparative material to draw conclusions on. Therefore it was decided to make some additional samples to be compared to the reference library. First some test samples of Derwent Studio pencils were made. These pencils are not watercolors, but the pigment names of the colors chosen were the same as those used in the watercolor references (Derwent, 2011, p 16, Winsor & Newton, n.d.-b). The Derwent samples were made on the same paper as the references and tested in the same ways as the other unknown samples. The choice of using Derwent Studio instead of Derwent Watercolors was because of availability. The hope was that, since names of the pencil's colors matched those in the reference library, their chemical composition would be the same. As seen below, this is not necessarily the case. Therefore some further samples of Winsor & Newton Artists' Water Colour tubes were made. The colors chosen were those which were available and which had the same name as the reference pigments. Together all the results will be used here to evaluate if the VSC can be used for pigment identification, and if so, which of its functions is best suited for the purpose.

7.1 Visible image

Comparison with the visible images did not give accurate results in all instances. "Old wife" did not look like French Ultramarine, but was similar to Prussian Blue. "A sailor" did not resemble any of the colors much, but French Ultramarine and Cerulean Blue were most similar. "Bondensen" looked like Burnt Umber but "The musicband" did not have as strong a resemblance. Both of the greens looked like Oxide of Chromium, but these were both mixtures of colors (Appendix 1, fig 1-5. Appendix 2, fig 6-19). Still these last comparisons cannot be counted fully, as there were no correct references to compare them to. If the reference library had mixed green colors to compare them to, they might look closer to these colors than to Oxide of Chromium.

The visual comparisons of the images were not done on the computer but with the images printed out on paper. A comparison of the image taken with the original image showed that the color renderings were off. The color renderings were not perfect on the computer screen either. Therefore a picture was taken of all the references with a standard color control strip. This will show how off the colors in the picture are from the actual sample. Still it is difficult to gauge the extent of this change visually when comparing colors. If one takes a picture of the unknown sample under the same conditions as the picture of the references, their color should in theory be off by the same amount, and therefore comparable. This was done in this experiment. Comparing the reference images directly with the original painting should not be done.

Taking all of the above into consideration the conclusion is that comparing colors visually can give false results, and cannot be used as an analytical method to identify pigments.

7.2 UV-image

None of the aquarelles had any visible fluorescence. Neither did any of the references, with the exception of Indigo, and here only in UV radiation with the wavelength of 312 nm. The areas in the reference, with the highest concentration of pigment, did not fluoresce as much as those with lower concentration. As none of the unknown pigments proved to be Indigo it was not tested if it could have been an identifying marker. The paper has some fluorescence by itself, and this can be seen especially at the edges of the water stains. Whether this fluorescence has affected the fluorescence seen with Indigo is unknown (Appendix 3, fig 11, 12).

As neither the samples nor references had any fluorescence it was like comparing black and white photographs. Comparing images this way did not lead to any exclusion of which pigments the paint could consist off. Therefore the UV-images were of no help to identifying the pigments present in the aquarelles.

With that said, if some of the references or samples had clear fluorescence, this might have been useful. It could have been used not as a single identifying marker, but more for excluding those with or without fluorescence. It is mainly organic pigments which fluoresce, and the fact that here was only one organic pigment in the reference library this is one reason why the method was not useful in this experiment. Therefore I would not rule out this method of comparison later on with a more comprehensive reference library.

7.3 Visible Spectra

With the visible graphs it turned out that only the unknown blues could be used to validate if the VSC's spectral function with visible light could be used for pigment identification. The greens were both mixtures and the browns could not be identified closer than to earth colors. The two blues proved to be the same color, French Ultramarine. The fact that there was only one certain pigment, made it hard to evaluate the VSC properly. Therefore the other samples made of the Derwent pencils and the Winsor & Newton tube colors were used.

7.3.1 Blues

Both the blues from the Zaitzow aquarelles had visible spectra that looked like French Ultramarine, and the SEM proved this correct. A further indication that they were the same color, and that this method of identification is valid, is that the two unknown graphs looked similar. It can be mentioned that Prussian Blue had a similar graph in shape but the areas of rise and fall were not located in the same areas (Appendix 4, fig 13, 14).

Derwent Studio colors of Ultramarine, Prussian Blue and Cobalt Blue were compared with the reference library. The Derwent Ultramarine and Derwent Prussian Blue had very similar graphs. Although the graphs in the reference library are not totally unlike each other, and one could thus expect some similarities, these were strikingly similar (Appendix 4, fig 19). In addition, the reference they looked most like was Indigo, and the graphs bore little resemblance to Prussian Blue. The Derwent colors had some similarities with French Ultramarine, but they had a small peak around 660 nm, which French Ultramarine lacks. If one looks close, however, there might be a small indication of a peak at around 660 nm in the graph recorded from the area of light pigment concentration in French Ultramarine. The first peak in the Derwent colors graph, at 410 nm, is most similar to French Ultramarine though, and maybe the colors are a mixture of French Ultramarine and Indigo.

The Derwent Cobalt Blue graph had similar shape as the Winsor & Newton Cobalt Blue but the graph looked more stretched so that the peaks were not in phase. The spectrum which

looks most like the spectrum of Derwent Cobalt Blue is again Indigo (Appendix 4, fig 20). The amount of changes in intensity is a bit off, but other than that, the graphs are very similar (Table 7).

Since the comparative results from the Derwent colors were questionable, samples from aquarelle tube colors from Winsor & Newton were made. Here the French Ultramarine looked almost identical to the reference French Ultramarine, and Prussian Blue looked like the reference Prussian Blue (Appendix 4, fig 23, 24. Table 8). Though probably with different additives, it is to be expected that the pigments used in the tube and pan colors are the same as they were both made from Winsor and Newton.

7.3.2 Browns

The SEM could not firmly identify the brown color in "The musicband" or "Bondensen" aquarelles any closer than earth colors. Most likely they are Umbers or Siennas. The graph of "Bondensen" looked like the Burnt Umber graph (Appendix 4, fig 15). For "The musicband" the results from the VSC indicated either Sepia or Burnt Umber. So, if the color is from an earth pigment, it is probably Burnt Umber. If a SEM examination was not done, the results from the VSC would not be conclusive, as Sepia also had a close resemblance to the unknown pigments graph (Appendix 4, fig 16).

It should also be mentioned that the burnt and raw form of the graphs of the Siennas and Umbers are similar, but there are some small differences. The graphs for the Siennas and the Umbers also look quite similar, but in general the Umber graphs are a bit flatter. These similarities can lead to ambiguities when trying to compare these graphs with an unknown sample.

Earths will also be somewhat different to each other as the earth they are gathered from will never be completely identical. This can lead to variations in the spectrums, and make the reading more difficult. All the earths also have similar elemental composition. They are all iron oxides. The other brown pigments used in the reference library are iron oxides as well. This might be a reason why some of the graphs have similar features, and the VSC might not be able to separate pigments with such similar composition properly.

The Derwent colors Raw and Burnt Sienna had basically identical graphs only with slightly different intensities. These looked most like Raw Sienna of the Winsor & Newton colors. The Derwent Raw and Burnt Umber also have similar graphs, but with different intensities. Although it was hard to tell, they might look most like Raw Umber (Appendix 4, fig 21, 22. Table 7).

The only brown tube color tested was Burnt Umber. The graph of this Burnt Umber looked most like the references Burnt Umber (Appendix 4, fig 25. Table 8).

7.3.3 Greens

As both of the green colors from the aquarelles proved to be mixtures, these could not verify if the visual spectrums are a viable comparative method other than the fact that they did not give false positives. Because none of the Derwent colors had the same name as the greens used in the Winsor & Newton references, no Derwent greens were tested. From the tube colors a sample of Terre Verte was made. The similarities of this graph to the reference Terre Verte was very close (Appendix 4, fig 26).

Table 7: The name of the Derwent Studio pencils measured, and the pigments in the reference library they looked most like.

Derwent Studio pencils	
Derwent Studio pencils	**Reference library pigments**
Ultramarine	Indigo
Prussian Blue	
Cobalt Blue	
Raw Sienna	Raw Sienna
Burnt Sienna	
Raw Umber	Raw Umber
Burnt Umber	

Table 8: The Winsor & Newton Artists' Water Colours measured and the pigments in the reference library they looked most like.

Winsor & Newton Artist's Water Colours (tubes)	
Tube colors	**Reference library pigments**
French Ultramarine	French Ultramarine
Prussian Blue	Prussian Blue
Burnt Umber	Burnt Umber
Terre Verte	Terre Verte

The visible spectrum is a method that shows promise in identifying pigments. It correctly identified both the blues from the aquarelles, in addition to all of the Winsor & Newton tube colors. The browns were harder to identify. The brown of "The musicband" looked like Burnt Umber, but without knowing that it was an earth pigment, it could have been misinterpreted as Sepia. The greens, which were mixtures did not give false positives.

The Derwent colors had similar names as the pigments from Winsor & Newton, but their graphs did not match their counterparts in the references. Their actual composition is unknown, but from the graphs of the blues it looked like the pigments used are different from what their names imply. The Derwent browns on the other hand look like they are Siennas and Umbers. Since their graphs were so similar it can look like the burnt colors have not been burnt, or that they have not been burnt as much as the Winsor & Newton colors. Another reason why the spectra did not match, could be that the binder used in the Derwent Studio pencils is different from the gum arabic in watercolors (Derwent, n.d.). How much the binder affects the spectra is not known, but it is an area that could be looked into more closely.

7.4 UV-spectra

None of the references except Indigo showed any visible fluorescence in their UV-images. However, they all had fluctuations in the spectra taken with UV radiation. Therefore there might be some fluorescence that the images do not show. UV spectral measurements of the plain white paper used for the references showed high fluctuations, and from the UV images taken, it has been seen that the paper has some fluorescence. Therefore, it might be possible that the fluorescence measured in some of the references has been caused by the papers fluorescence.

Some of the characteristics of the UV-spectra are that they all have several peaks and troughs. In addition the graphs are ever-changing. The graphs registered are just one version, and if one had waited a couple of seconds to copy the graph, it would probably look a bit different. The UV-function records visible fluorescence when irradiated by UV radiation. This makes the spectra small, since it starts around 425 nm and ends around 700 nm. All the factors above make it hard to read and compare the graphs.

Another feature that is worth mentioning is that the graphs do not always look alike when taken with the same wavelength, but in different areas of pigment concentration. Thus an unknown sample can look, for example, like the middle area indigo, but not like its dark area. This makes interpretation harder.

When looking at some of the samples from the image of "A sailor", it has in UV 365 similarities to French Ultramarine. However there is a marked top in the sample which is not present in the reference. In addition the same graph bears resemblance to both Cerulean Blue and the paper spectra. The UV 312 spectrum has lower intensity than that taken with 365 nm. This too bears resemblance to Cerulean Blue and the paper but less than the previous to French Ultramarine (Appendix 5, fig 27-30).

The spectrum taken with the wavelength of 365 nm of "Old wife" does not look as alike as that of "A sailor" as one might expect, although there are some similarities. Other than that it looks a little like Cerulean Blue. There is some likeness to French Ultramarine and the paper spectra, but this is not as high as "A sailor" had. In 312 nm the measurement looks more like French Ultramarine than it did with 365 nm.

The French Ultramarine tube color taken with 365 nm and 312 nm can look like the references French Ultramarine but also like Cobalt Blue and a little like Prussian Blue. The tube color of Terre Verte also gives uncertain results, and is not strikingly similar to the reference graphs of Terre Verte, but it could look a little like Cobalt Green.

How many similarities must be present to say when two graphs look alike is difficult to say. A question is also if it is enough with a match only in on area of pigment concentration to identify a pigment, or if there must be similarities to other areas of differing pigment concentration as well? Thirdly it is unclear if one can make a match with spectra from only one wavelength or if spectra from different wavelengths must match as well. Since it is hard to interpret the spectra and that they can look like more than one pigment, this proves that this method of pigment identification does not work. Because the graph changes with time and the graph recorded is just one of many, comparison is not based on a good foundation, and can thus be said to be futile.

7.5 Spot (fluorescence)

When choosing which filters to use in the Spot (fluorescence) function, it was decided to use three different filters which were equally spaced from each other in the hope that with their different wavelengths, they would provide useful information for pigment identification. The thought of using the function as it is without a specific filter was considered. Then the spot would shine visible light on the sample and the camera could admit energy in or close to infrared. When testing this it was revealed that the graph from this measurement was in many cases very like the graph received from measuring with the yellow filter (Fig 8). Therefore, this was considered redundant.

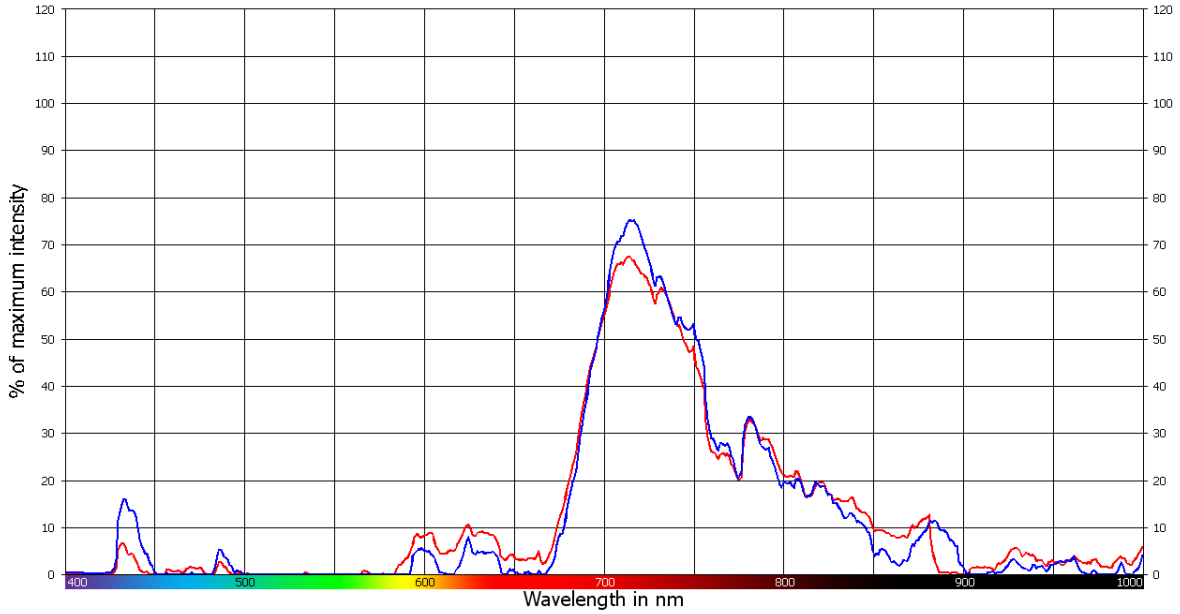

Figure 8: These graphs show the similarities between Burnt Sienna measured with a yellow spot, and the graph measured without using a filter in the Spot (fluorescence) function.

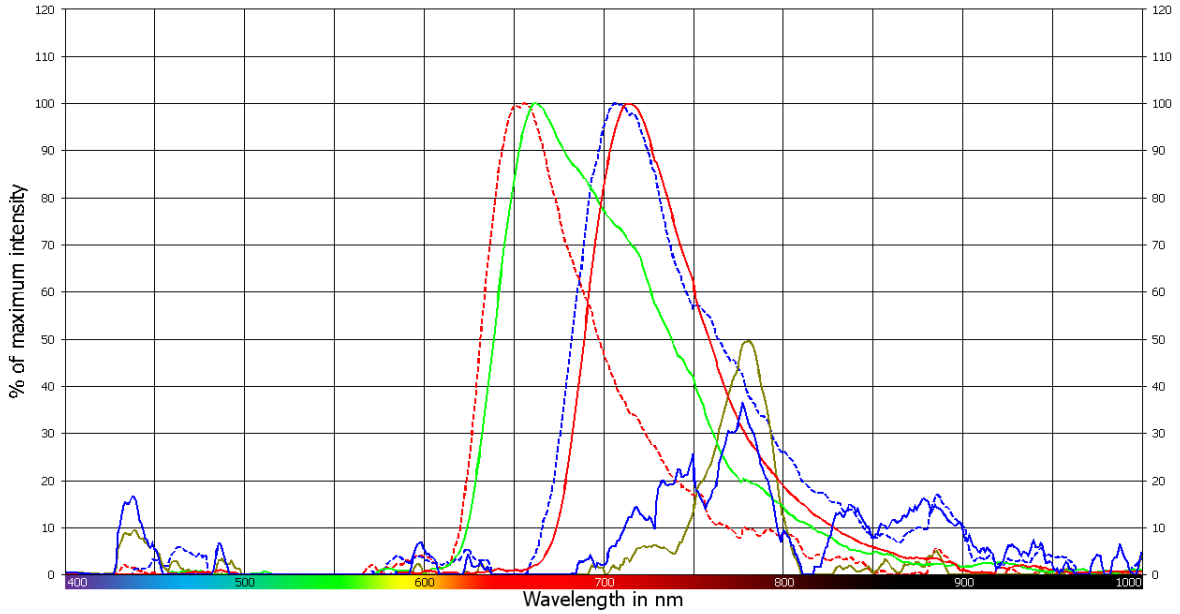

Figure 9: The measurements taken from the light area of pigment concentration from "A sailor", and measurements taken from plain paper.

The spot measurements of the references have been, as with visible light and UV-light, taken in three different areas of pigment concentration. A reason for this was that the pigment concentration in various samples will never be the same, and in theory this would give a better chance for a match. When comparing the reference's measurements taken from areas of light pigment concentration, they often looked much like the measurements taken from plain paper (Fig 9). The reason for this might be that the paper shines through in the areas of light

pigment concentration. The similarity in some references is so high that it is possible that it is the paper that contributes most to the graphs. If this is the case, the references measured from the areas of light pigment concentration do not reflect the pigment and thus cannot be used in the analysis. Therefore, they have been excluded from further consideration.

It is possible that unknown samples with light pigment concentration, if measured, will also reflect their paper and not as much their pigment. In such cases identification may not be possible unless an area of higher pigment concentration can be selected for analysis.

The spectrum taken from "Old wife" has a likeness to the paper samples spectrum. In "Old wife" measurements were taken only in one place, and in an area of presumably high pigment concentration. There is a possibility that the paper still shone through, or that the area measured was not representative, and that this is the cause of the similarities. But the graph from "Old wife", taken with the blue filter, has an extra small peak around 730 nm. The red filter graph measured, has much less intensity, and more peaks than the graph measured from the plain paper. The French Ultramarine references did not look much like the graphs from "Old wife". The most alike were the ones taken with the red filter. The blue filter graph from the middle area can have some similarities with the samples, but the resemblance is not high. It also looks like the middle area graph from the Indigo reference (Appendix 6, fig 31, 33, 35).

The light area measurements from "A sailor" looked like the paper spectrum. Excluding these measurements, "A sailor" had some similarities with the Prussian Blue middle area, Indigos dark area and Cerulean Blues middle area. It did not really resemble French Ultramarine (Appendix 6, fig 32-33, 34-35).

The French Ultramarine spectra from the Winsor & Newton tubes, looked like many of the reference spectra, among them French Ultramarine. Which one is most alike is difficult to determine, and will not be attempted here.

With the earths the raw and burnt form has similar characteristics in both Sienna and Umber. This fact leads one to believe that the graphs can show characteristics of the pigments and thus can be used for identification. The graph from "The musicband" also has likeness to these graphs but then most to Raw Sienna, Raw Umber and Burnt Umber. The likeness is not 100% but there are strong similarities (Appendix 6, fig 38-39, 41). "Bondensen", which looked like Burnt Umber with the visible spectra, does not look much like the earths in the Spot (fluorescence) function.

The Burnt Umber tube from Winsor & Newton looks, if one must choose, most like Burnt Umber from the references, but again the similarities are not striking. The Terre Verte tube color's spectrum has a likeness to the reference Cobalt Green, but there are also some similarities to Terre Verte.

As seen with the compared graphs above, the results are ambiguous. In one instance, it looks like the method is pigment specific and can be used to identify pigments. In other instances, it does not seem like it. When the graphs are alike, they are never 100% similar. Some of these deviant results might be because of faults in the measurements. The area chosen might not have been representative of the pigment in that the paper might have shone through, there might have been impurities present, the pigment might have deteriorated or it might have been mixed with other pigments.

It is hard to determine if the Spot (fluorescence) function can be used or not to identify pigments. As a result of this experiment, I would say that the method is not suited. One of the

main problems is that there is too much information to process just by visual inspection. With a specially designed computer program which can match graphs and calculate the percentage of the matches it would be easier to use and evaluate the spot (fluorescence) function.

In this experiment SEM-EDS was the only other identification method that was used. If one of the pigments had turned out to be organic, this could have been a problem, as SEM can only identify inorganic pigments. Therefore, it could have been useful to have had another method available which could have identified organic pigments. From chapter three it is shown that it is mostly the methods that work in the infrared region that can identify organic pigments and dyes. So in this case FTIR, Raman, FORS and THz spectroscopy could have been helpful. Since there also were problems with identifying the brown colors, another method might have been more helpful. XRD for instance, can identify the crystal structure, and thus distinguish between pigments with similar chemical composition.

7.6 Conclusion

The VSC can most likely be used for pigment identification, but as seen above not all of the functions are suitable. Of the five functions tested, it is the Visual spectra which gave the most correct results. The functions of the visible image and UV-spectra proved not to be useful. The visible image did not give correct answers when the French Ultramarines were compared, and it also gave false positives with some of the other colors. The UV-spectra was difficult to read and since the live spectrum keeps changing, the one recorded will be only one version. Therefore it is difficult to compare these spectra. The UV-image and the Spot (fluorescence) functions did not help much in this experiment, but they might prove more useful later on. The UV-image can probably be useful, to eliminate many possible pigments, if the reference library is larger. The Spot (fluorescence) function on the other hand needs further evaluation. One of the problems is to know how much alike the graphs should look to be considered a match. Another problem is that in this function there is a lot of information, so errors are easily made. To change this one could possibly reduce the number of measurements taken from each sample. It might also help to have a computer program that can calculate matches, and thus make the comparisons more objective. Whether these measures prove that the method can be used for pigment identification, this is an area that could be studied further.

The spectral graph function with visible light has the largest potential for being a method for pigment identification. The readings from it in this experiment proved to be fairly accurate. However, the experiment showed one area that can become an issue. One of the pigments that might be Burnt Umber had a graph that could also look like Sepia. The browns in the reference library all have iron oxide in them, something that might cause similarities in the graphs. It was seen that some of these graphs were difficult to distinguish from each other. Hence, this method of pigment identification should be tested further with more pigments before a final decision on its validity for pigment identification is made.

In this experiment mainly watercolors were used. The Derwent Studio pencils are not watercolors, and it turned out that they did not match the watercolor references well. One reason could be that the pencils contain different pigments than the color’s name implies, but it is also possible that the binder used has a strong effect on the spectra measured. It would be interesting to examine other paints that are not watercolors, such as oils, to see how much the binder affects the spectrum. Can one reference library be used for all types of painting techniques or must references be made for each pigment with the different binders possible?

To summarize it can be concluded from this experiment that the VSC most likely can be used for pigment identification. Further tests should be done, however, as the test material used here is not large enough to give certain answers. In addition it should be pointed out that since the VSC is a comparator and not an analytical instrument, it is not calibrated as an analytical instrument either. Results from it are indicative and not definite. Therefore, if one needs certain results, tests should also be done with another instrument. Organic and inorganic mediums can sometimes best be analyzed with different instruments. From this it can be reasoned that it is useful to have several methods of identification available. If, with further tests, it is confirmed that the VSC is reliable at pigment identification, this method will only be one of many possible. Since it is a comparator and not an analytical machine, results will never be 100% certain with the VSC, but by having other features that can be useful in a conservation studio as well, the VSC might still have a valid place within the cultural heritage sector. As many colors are made by mixing pigments, it should be tested if the VSC can identify these. If it cannot, its use for pigment identification may be limited.

The amount of data to compare is large and even with a small reference library visual comparison is difficult. As seen mostly with the Spot (fluorescence) function, it was difficult to say which graphs are most alike the unknown sample's. If one chooses to expand the reference library there will be too much data to process by visual examination alone. Therefore visual examination of the graphs might not be the most reliable method of comparison. Subjective opinions are individual, and can alter with the person's state of mind. And when too many graphs are compared, it is hard to keep track of them all. A computer program would help to remove the subjective opinions, and one can decide how much alikeness there must be between graphs to constitute a match.

8. Summary

The Video Spectral Comparator 6000 (VSC) by Foster + Freeman is a machine used traditionally as a forensic tool to investigate documents to see if they are authentic or forgeries. It is also used to some extent in the cultural heritage sector, to look at documents. Here the use has expanded to include, among other things, evaluation of dyes, degradation of paper and characterization of color. While I was an intern at the National Library of Oslo, Norway, I came in contact with this machine. It was suggested to me that it would be interesting to find out if the machine could be used to identify pigments non-destructively, and as my undergraduate thesis I chose to explore this subject. For the purpose, a collection of aquarelles from 1929 by Alexey Zaitzow was made available for me to use as test material.

Absorption and reflection of light is what gives us the sensation of color. What is reflected, absorbed or transmitted is dependent on many factors, but the most important is the atom or molecule itself. The different wavelengths in the electromagnetic spectrum behave differently with atoms and molecules. While the longer wavelengths, such as Infrared (IR) can only cause rotation and vibration in molecules, the higher energy wavelengths can excite electrons and even expel them from the atoms. Spectroscopy is a method where one shines a light on a sample and registers the absorbed, transmitted or emitted light from the sample. It uses the atoms and molecules characteristic binding energies to gain information on either the elements present in a sample or of how elements are combined. Sometimes, with some techniques, one can also get information of the amount of elements present in an area. Most analytical instruments are based on spectroscopy.

There are many analytical instruments on the market today that are used to identify pigments. Many of these are non-destructive to the material they are analyzing or can be made non-destructive. A description, in this paper, of some of the most commonly used instruments, showed that all of these have their advantages and disadvantages.

This experiment was done by first making a reference library of 15 watercolors. These colors were chosen, as representing the blue, brown and green colors most used in the 1920s. The references were documented in the VSC with five functions. These were Visual image, UV-image, Visual spectra, UV spectra and Spot (fluorescence) spectra. Then six different colors from the Zaitzow aquarelles were documented in the same way. These were then compared to the references. Samples were also taken from the aquarelles and analyzed with a Scanning Electron Microscope (SEM). The SEM can give more certain results of the pigment composition, and was therefore used to validate or invalidate the compared results. As it turned out the two blues proved to be French Ultramarine and the browns earth colors, probably Burnt Umber. The greens were mixtures. Since this was seen as insufficient material to draw firm conclusions, additional samples were made with Derwent Studio color pencils and tube colors from Winsor & Newton.

The results from the comparisons revealed that not all of the tested functions can be used to analyze pigments. The visual image and the UV-spectra were most inadequate. The tested pigments did not always look like the equivalent pigments in the visual images. The UV spectra proved difficult to read as there were so many peaks and troughs in a small area. This made the spectra hard to compare, but the main factor that made the method inadequate is that the graphs kept changing. The recorded spectrum is just one version of the graph, and had one recorded it a few seconds before or after, it would have changed.

The UV-image and Spot (fluorescence) methods were not very useful in this experiment, but can probably be made more useful later on. In the UV-images taken from the references, only one reference, Indigo, fluoresced. None of the unknown pigments fluoresced either, so this only proved that none of them were Indigo. By adding more pigments in the reference library, this function can be used as a tool to eliminate many possibilities when trying to identify an unknown pigment. The Spot (florescence) function was also hard to read. This is partly because there was much information to process, and keep tabs on, when comparing spectra. Sometimes it was difficult to say which spectra looked most like the unknown pigments. Also it was seen that the measurements taken from an area of light pigment concentration, looked much like measurements taken from plain white paper. Therefore these measurements may not be helpful in identifying pigments. To overcome these problems, it might help to input the data in a computer program which can mathematically calculate matches. This might prove that the method can be used for pigment identification, but there is also a possibility that it proves that the Spot (fluorescence) function is not useful for this purpose.

The function which shows most promise is the Visual-spectra. In almost all cases, the tested pigments looked most like the equivalent reference spectrum. It was mainly the Derwent colors that did not match. The reason for this might be that their pigment composition is not what the colors name implies. All of the tube colors from Winsor & Newton and the blues and the browns from the original samples matched their corresponding reference.

The conclusion is that the VSC can most likely be used for pigment identification. And of the five functions of the VSC tested, the visual spectral measurement function shows most promise. To make certain one should expand the reference library and make further tests. Mainly watercolors have been used in this experiment, so it would be interesting to see if the results are different with other painting techniques, such as oils. As the comparisons in this experiment have been made visually, the conclusions can be drawn into question. Because of this, and because not all of the functions tested could give indications if they could be used for pigment identification, it might be helpful to make a computer program which could compare graphs. This would be especially useful for the Spot (fluorescence) function, in which the amount of data was large.

Definitions

Isotropic: An isotropic pigment has identical properties in all directions.

Anisotropic: An anisotropic pigment does not have identical properties in all directions.

Broadband radiation: Broadband radiation is radiation which has a broad and continuous spectrum of frequencies. A filament lamp has broadband radiation. Such radiation is often used in spectroscopy (Encyclopædia Britannica, 2011).

Narrow-band radiation: Narrow-band radiation is, in contrast to broadband, radiation form a defined range of frequencies. A laser, for example, uses narrow-band radiation (Encyclopædia Britannica, 2011).

Polarized light: A beam of light has waves that can have different amplitudes and orientations in space. It can basically take three forms which are known as linear, circular and elliptical polarized light. When the beam of light hits a surface some of these ways of moving are suppressed and the beam becomes polarized. In some analytical techniques one can selectively polarize light to see characteristics of pigments (Brill, 1980, pp 47-50, Mazzeo et al., 2009, p 181).

Longpass camera filter: a longpass camera filter hinders shorter wavelengths from entering the camera, while letting light with longer wavelengths pass into the camera and become recorded. In the VSC it lets light from around 610nm-1000nm pass. This kind of filter is often used when viewing fluorescence or infrared light (Foster + Freeman, 2009, p 48).

Shortpass camera filter: A shortpass camera filter, in the VSC, only lets light in the visible range of the electromagnetic spectrum pass into the camera (Foster + Freeman, 2009, p 48). Other shortpass filters can also let some UV light pass.

Transflection: “Transflection occurs on thin films of sample spread on a smooth metal surface. In this situation the radiation is transmitted through the sample, reflected by the metal surface and transmitted again through the sample.” (Brunetti et al., 2009, p 157).

Tristimulus values: The Tristimulus values are three coordinates in a color chart which indicates how much of the three primary colors must be mixed to get a specific color (Taft et al., 2000, pp128-130).

Bibliography

Printed sources

ASHER, S. A. 2002. Ultraviolet Raman Spectrometry. *In:* CHALMERS, J. M. & GRIFFITHS, P. R. (eds.) *Handbook of Vibrational Spectroscopy.* Chichester: John Wiley & Sons Ltd.

BACCI, M. 2006. Non-Invasive Instrumentation for Detection and Colour Control of Paintings and Art Works. *Archeometriai Műhely***,** pp 46-50.

BACCI, M., BOSELLI, L., PICOLLO, M., PRETZEL, B. & RADICATI, B. 2009. Colorimetry. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 143-146.

BARKER, W. & FOURNELLE, J. 1996. X-ray Compositional MicroAnalysis: EDS and WDS. *Electron Microscopy: Theory and Practice.* Madison, WI: University of Winsconsin-Madiosn, Anatomy Department, Anatomy 660.

BELLOT-GURLET, L., PAGÈS-CAMAGNA, S. & COUPRY, C. 2006. Raman Spectroscopy in Art and Archaeology. *Journal of Raman Spectroscopy,* Vol 37**,** pp 962-965.

BOMSDORF, H. 1999. Coherent X-Ray Scatter for Non-Destructive Testing of Works of Art. *6th World Conference on NDT and Microanalysis in Diagnostics and Conservation of Cultural and Environmental Heritage.* Rome: AIPnD.

BRILL, T. B. 1980. *Light: its interaction with art and antiquities,* New York, Plenum Press.

BRUNETTI, G. B., MILIANI, C., ROSI, F. & SGAMELLOTTI, A. 2009. Fourier Transform Infrared Spectroscopy (FTIR) by fiber optics. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 157-158.

BUSSOTTI, L., CARBONCINI, M. P., CASTELLUCCI, E., GIUNTINI, L. & MANDÒ, P. A. 1997. Identification of Pigments in a Fourteenth-Century Miniature by Combined Micro-Raman and Pixe Spectroscopic Techniques. *Studies in Conservation,* Vol 42**,** pp. 83-92.

BUZZEGOLI, E. & KELLER, A. 2009a. Ultraviolet fluorescence imaging. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 204-205.

BUZZEGOLI, E. & KELLER, A. 2009b. Ultraviolet/Infrared false colour imaging. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 200-203.

CASINI, A., LOTTI, F., PICOLLO, M., STEFANI, L. & BUZZEGOLI, E. 1999. Image Spectroscopy Mapping Technique for Non-Invasive Analysis of Paintings. *Studies in Conservation,* Vol 44**,** pp 39-48.

CASINI, A., LOTTI, F., POGGESI, M. & STEFANI, L. 2009. Imaging Spectroscopy (IS). *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 165-167.

CASTAING, J. & DRAN, J.-C. 2009. X-Ray Diffraction (XRD). *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 207-210.

DERWENT 2011. 2011 Derwent Catalogue. Cumbria: The Cumberland Pencil Company Ltd.

DERWENT n.d. Colouring Range Leaflet. *Cumberland Pencil Company Ltd.* Cumbria: Cumberland Pencil Company Ltd.
DOERNER, M. 1969. *The materials of the artist and their use in painting with notes on techniques of the old masters,* London, Hart-Davis,MacGibbon.
DRAN, J.-C. & LAVAL, E. 2009. X-Ray Fluorescence (XRF). *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 210-213.
DRAN, J.-C. & PAGÈS-CAMAGNA, S. 2009. Raman micro-Spectrometry. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 188-190.
FELLER, R. L. 1986. *Artists' pigments: a handbook of their history and characteristics,* Cambridge, Cambridge University Press.
FUKUNANGA, K., OGAWA, Y., HAYASHI, S. I. & HOSAKO, I. 2007. Tetrahertz spectroscopy for art conservation. *IEICE Electronics Express,* Vol 4**,** pp 258-263.
GALEOTTI, M., JOSEPH, E., MAZZEO, R. & PRATI, S. 2009. Fourier Transform Infrared Spectroscopy (FTIR). *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 151-154.
GENESTAR, C. & PONS, C. 2005. Earth pigments in painting: characterisation and differentiation by means of FTIR spectroscopy and SEM-EDS microanalysis. *Analytical and Bioanalytical Chemistry,* Vol 382**,** pp 269-274.
GETTENS, R. J. & STOUT, G. L. 1966. *Painting materials: a short encyclopaedia,* New York, Dover Publications.
HARRIS, D. C. & BERTOLUCCI, M. D. 1978. *Symmetry and spectroscopy: an introduction to vibrational and electronic spectroscopy,* New York, Oxford University Press.
HAYES, C., HALLSTRÖM, B. H. & HALLSTRÖM, D. (eds.) 1979. *Atlantis stora handbok i måleri, teckning och grafik: tekniker och material,* Stockholm: Atlantis.
HOCQUET, F.-P., GARNIR, H.-P., CLAR, M., OGER, C. & STRIVAY, D. 2008. A remote controlled XRF system for field analysis of cultural heritage objects. *X-Ray Spectrometry,* Vol 37**,** pp 304-308.
HOLLAS, J. M. 2004. *Modern spectroscopy,* Chichester, Wiley.
HOSAKO, I., KOHDZUMA, Y., KOEZUKA, T., KIM, M.-J., IKARI, T. & DU, X. 2010. Tetrahertz analysus of and East Asian historical mural painting. *Journal of the European Optical Society,* Vol 5**,** pp. 1-4.
INEKE, J. & SPRING, M. 2009. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS or EDX). *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 191-193.
KLOCKENKÄMPER, R., VON BOHLEN, A. & MOENS, L. 2000. Analysis of Pigments and Inks on Oil Paintings and Historical Manuscripts Using Total Reflection X-Ray Fluorescence Spectrometry. *X-Ray Spectrometry,* Vol 29**,** pp 119-129.
MARTIN, M. C., SCHADE, U., LERCH, P. & DUMAS, P. 2010. Recent applications and current trends in analytical chemistry using synchrotron-based Fourier-transform infrared microspectroscopy. *Trends in Analytical Chemistry,* Vol 29**,** pp 453-463.
MAYER, R. & SMITH, E. 1987. *The artist's handbook of materials and techniques,* London, Faber.
MAZZEO, R., PRATI, S. & SANDU, I. 2009. Optical Microscopy. *In:* PINNA, D., GALEOTTI, M. & MAZZEO, R. (eds.) *Scientific Examination for the Investigation of Paintings. A Handbook for Conservator-restorers.* Florenze: Centro Di, pp 179-183.

MERRIFIELD, M. P. 1967. *Original treatises on the arts of painting,* New York, Dover Publications.
MOIOLI, P. & SECCARONI, C. 2000. Analysis of Art Objects Using a Portable X-Ray Fluorescence Spectrometer. *X-Ray Spectrometry,* Vol 29**,** pp 48-52.
PEREZ-PUEYO, R., SONEIRA, M. J. & RUIZ-MORENO, S. 2004. A fuzzy logic system for band detection in Raman spectroscopy. *Journal of Raman Spectroscopy,* Vol 35**,** pp 808-812.
PINNA, D., GALEOTTI, M. & MAZZEO, R. 2009. *Scientific examination for the investigation of paintings: a handbook for conservators-restorers,* Florenze, Centro Di.
ROY, A. 1993. *Artist's pigments: a handbook of their history and characteristics : volume 2,* Oxford, Oxford University Press.
SCHREINER, M., MELCHER, M. & UHLIR, K. 2007. Scanning electron microscopy and energy dispersive analysis: applications in the field of cultural heritage. *Analytical and Bioanalytical Chemistry,* Vol 387**,** pp 737-747.
SMITH, G. D. 2003. Infrared Microspectroscopy Using a Synchrotron Source for Arts-Science Research. *Journal of the American Institute for Conservation,* Vol 42**,** pp 399-406.
STANG, KAARE, 2007. *Z for Zaitzow,* Norsk Filminstitutt.
TAFT, W. S., MAYER, J. W., NEWMAN, R., STULIK, D. & KUNIHOLM, P. I. 2000. *The science of paintings,* New York, Springer.
TATE GALLERY, 1982. *Paint & painting: an exhibition and working studio sponsored by Winsor & Newton to celebrate their 150th anniversar,* London, Tate Gallery.
VAN GRIEKEN, R. E. & JANSSENS, K. 2005. *Cultural heritage conservation and environmental impact assessment by non-destructive testing and micro-analysis,* Leiden, A.A. Balkema Publ.
WINSOR & NEWTON, 2005. Winsor & Newton Artists' Water Colour: Perfecting the Fine Art of Water Colours. Harrow: Winsor & Newton.

Internet sources:

CLARK, R. J. H. 2011. Raman Microscopy as a Structural, Analytical and Forensic Tool in Art and Archaeology. *Chemistry in New Zealand* [Online]. Available: http://yearofchemistry.org.nz/wp-content/uploads/2010/12/CiNZ-Jan2011_Clark.pdf [Accessed 6 May 2011].
ENCYCLOPÆDIA BRITANNICA, 2011. *Broadband* [Online]. Encyclopædia Britannica. Available: http://www.britannica.com/EBchecked/topic/1365587/broadband [Accessed 9 May 2011].
FOSTER + FREEMAN, 2011. *VSC®6000/HS* [Online]. Available: http://www.fosterfreeman.com/index.php?option=com_content&view=article&id=9&Itemid=28 [Accessed 18-03-2011].
GREAT ART. 2011. *Da Vinci Junior Synthetics Series 303* [Online]. Available: http://www.greatart.co.uk/DAVINCIJUNIORSYNTHETICSSERIES303-brushes-2.htm [Accessed 09-06-2011].
HANS SCHRÖDER, 2010. *Catalogue – Photographs,* Hans Schröder GmbH [Online]. Available: http://www.archiv-box.de/filestorage/1/1_803.pdf. [Accessed 18-03-2011].
HANS SCHRÖDER, n.d. *Hans Schröder GmbH,* Hans Schröder GmbH [Online]. Available: http://www.archiv-box.de/content.php?target=about&lang=en.
HARVARD GAZETTE, 2008. "Patricia Cornwell endows conservationist at Straus Center", *Harvard Gazette*, 4 December [Online]. Available:

http://news.harvard.edu/gazette/story/2008/12/patricia-cornwell-endows-conservationist-at-straus-center/ [Accessed 18-03-2011].
HERENDEEN, D. L. 2009. *A Colorimetric Analysis Methodology for Philatelic Studies*, sample proposal for the Smithsonian National Postal Museum 20 August[Online]. Available: http://analyticalphilately.org/images/SampleProposal.pdf [Accessed 18-03-2011].
IMAGE PERMANENCE INSTITUTE, 2011. *Photographic Activity Test (PAT),*Image Permanence Institute, Rochester Institute of Technology[Online]. Available: https://www.imagepermanenceinstitute.org/testing/pat [Accessed 18-03-2011].
LGC FORENSICS, 2011, *Video Spectral Comparator*, LGC Limited [Online]. Available: http://digital.lgcforensics.com/services/questioned-documents/video-spectral-comparator.html [Accessed 18-03-2011].
MICHELSEN, A.. n.d. *Knut Hamsun Online* [Online]. Available: http://www.hamsun.dk/uk/hamsun_boger.html [Accessed 18-03-2011].
MOKRZYCKI, G. M. 1999. "Advances in Document Examination: The Video Spectral Comparator 2000", *Forensic Science Communications*, vol. 1, no. 3, [Online]. Available: http://www2.fbi.gov/hq/lab/fsc/backissu/oct1999/mokrzyck.htm [Accessed 18-03-2011].
OSLO NYE TEATER, n.d. *Om Teateret: Historie* [Online]. Available: http://www.oslonye.no/om_teatret/historikk/ [Accessed 18-03-2011].
POLI, T., ELIA, A. & CHIANTORE, O. 2009. Surface Finishes and Materials: Fiber-Optic Reflectance Spectroscopy (FORS) Problems in Cultural Heritage Diagnsotics. *e-PRESERVATIONScience* [Online]. Available: http://www.morana-rtd.com/e-preservationscience/2009/Poli-03-07-2008.pdf [Accessed 09-06-2011].
SECURITY PRINTING, 2007. *Holograms and optical variable devices,* Security Printing.co.uk [Online]. Available: http://www.securityprinting.co.uk/holograms-ovds.php [Accessed 18-03-2011].
WINSOR & NEWTON, n.d.-a. *About us: The Winsor & Newton Story (1832-2007)* [Online]. Winsor & Newton. Available: http://www.winsornewton.com/about-us/our-history/ [Accessed 6 May 2011].
WINSOR & NEWTON, n.d.-b. *Artists' Water Colour: Compostion and Permanence* [Online]. Available: http://www.winsornewton.com/products/water-colours/artists-water-colour/composition--permanence/ [Accessed 6 May 2011].
WISNOR & NEWTON, n.d-c. *Artists' Water Colour: Further Information* [Online]. Winsor & Newton. Available: http://www.winsornewton.com/products/water-colours/artists-water-colour/further-information/#2 [Accessed 6 May 2011].

Figures and tables

Figures:

Tables:

Appendix

Appendix 1. The aquarelles by Alexey Zaitzow

Figure 1: "Old wife". The ring marks the area measured.

Figure 2: "A sailor". The ring marks the area measured.

Figure 3: "Bondensen". The ring marks the area measured.

Figure 4: "The musicband". The ring marks the area measured.

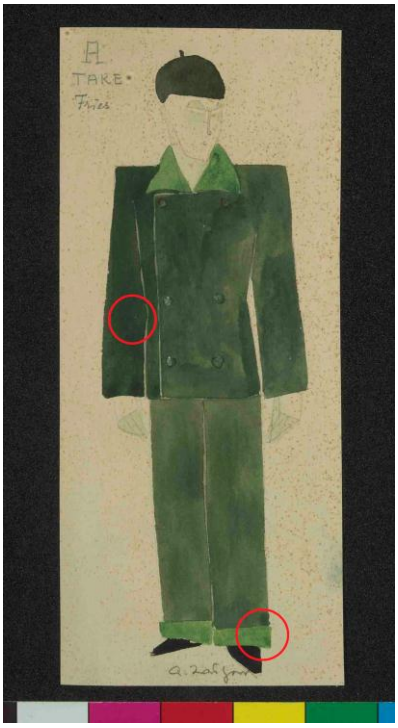

Figure 5: "Tare". The rings mark the areas measured

Appendix 2. Visual images of the refernces

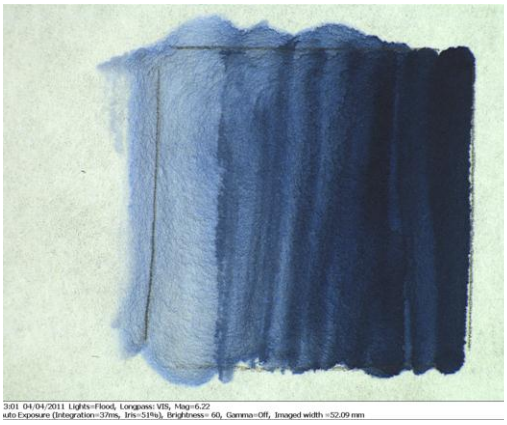

Figure 6: Indigo. Overview image taken with visible light.

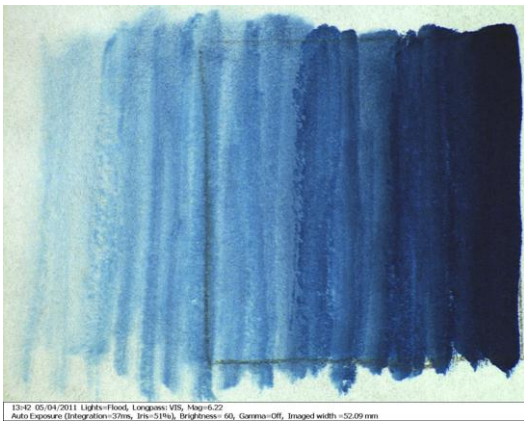

Figure 7: Prussian Blue. Overview image taken with visible light.

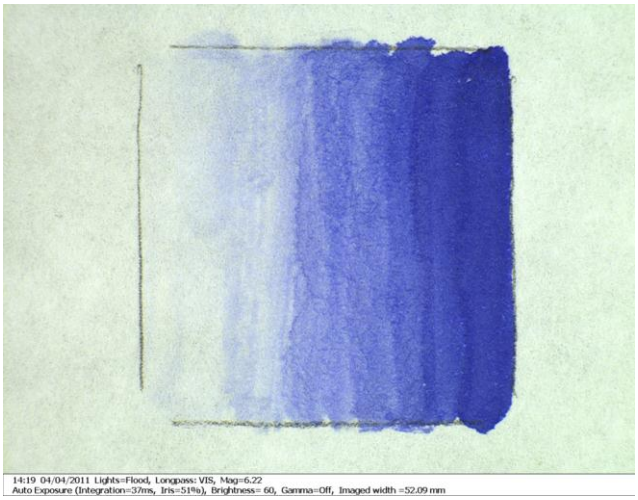

Figure 8: French Ultramarine. Overview image taken with visible light.

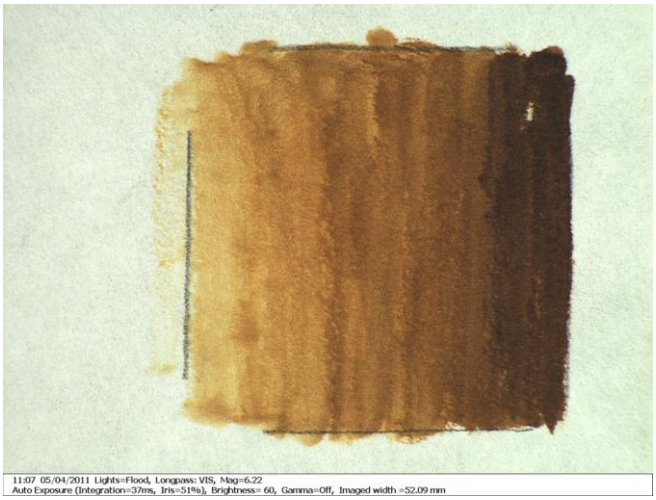

Figure 9: Burnt Umber. Overview image taken with visible light.

Figure 10: Oxide of Chromium. Overview image taken with visible light.

Appendix 3. UV-images

Figure 11: "Old wife". UV-365. No fluorescence is visible.

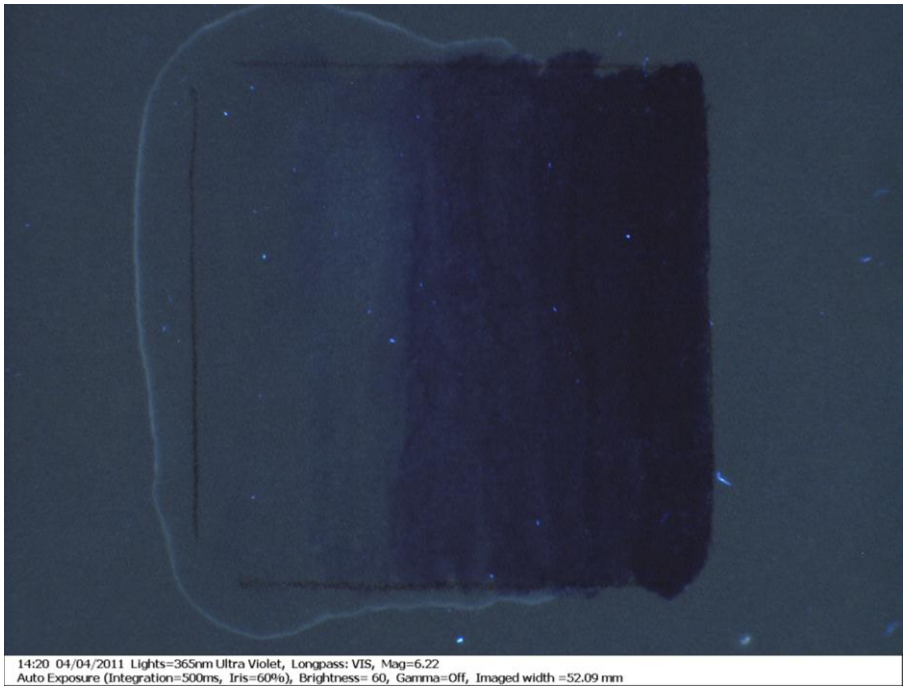

Figure 12: French Ultramarine. UV-365. No fluorescence is seen except in the waterstain.

Appendix 4. Visible spectra

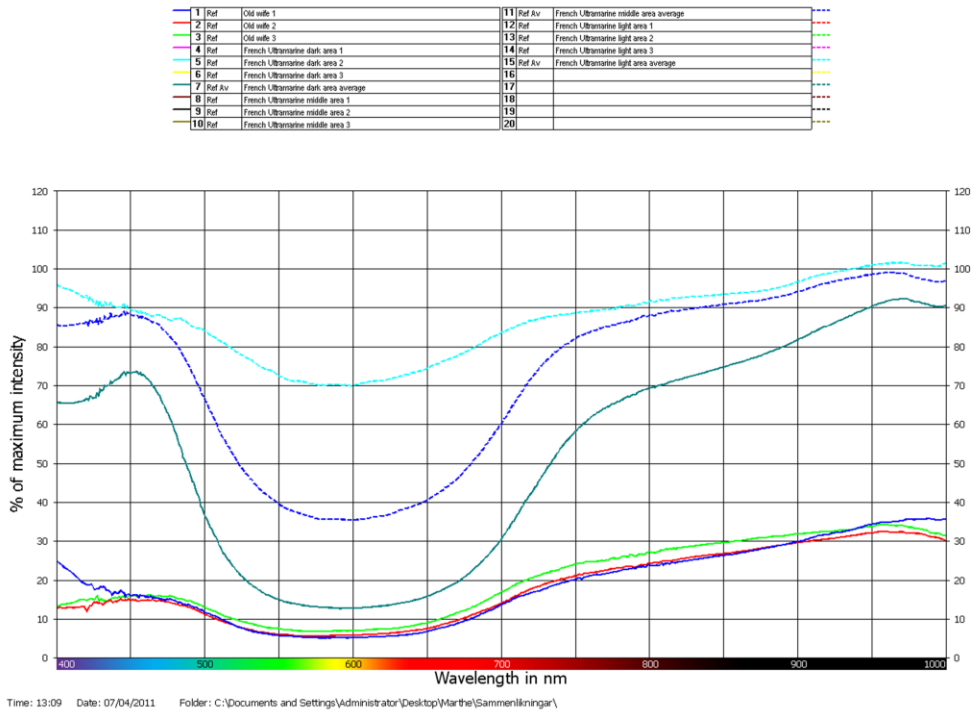

Figure 13: "Old wife"and French Ultramarine. The graph taken from the light area of pigment concentration looks most like the graphs from "Old wife". The bottom graphs belong to "Old wife". The remaining three graphs belong to French Ultramarine, with the light area graph highest up.

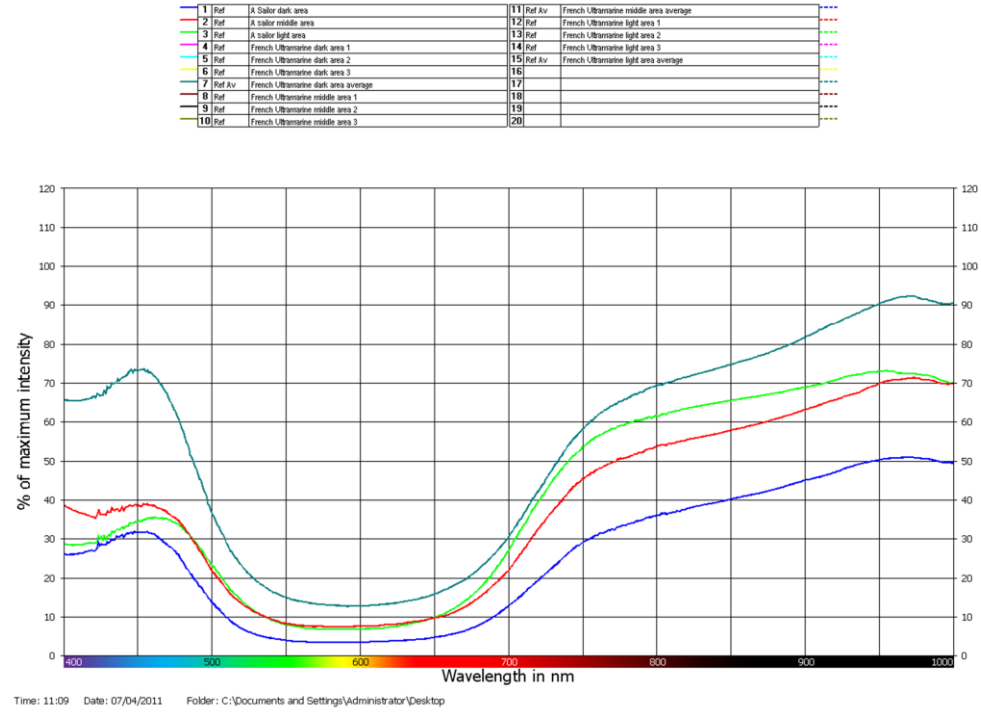

Figure 14: "A sailor" and French Ultramarine. The top graph is from the reference of French Ultramarine, the bottom graphs are measured from "A sailor".

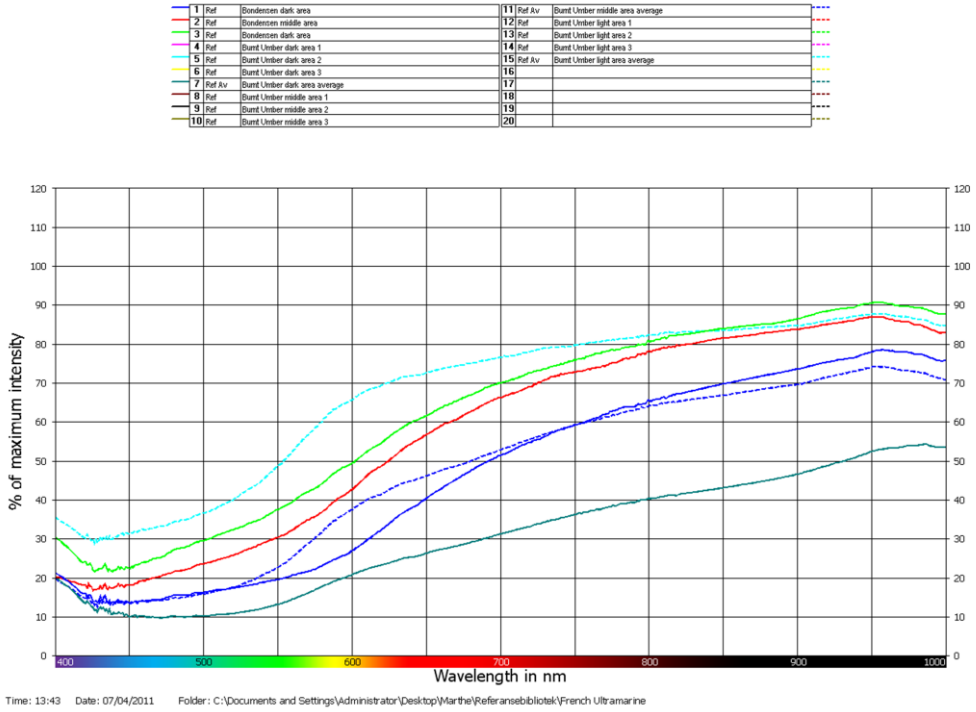

Figure 15: "Bondensen" and Burnt Umber. The red green and solid blue graphs belong to "Bondensen", and the light blue and two blue dotted lines are the averages from Burnt Umber.

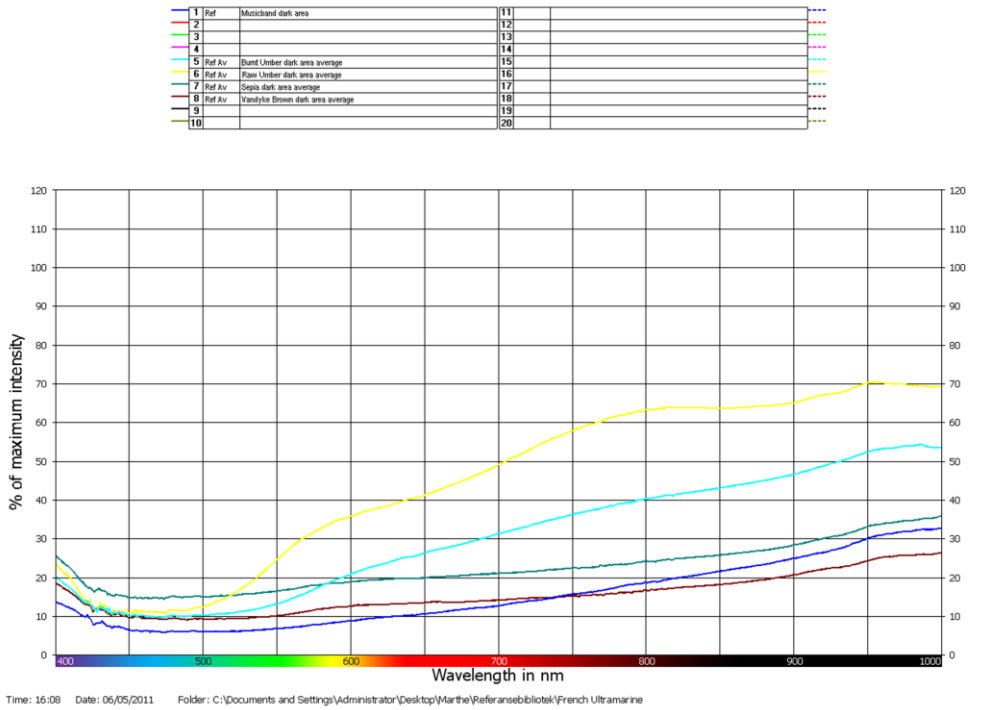

Figure 16: "The musicband" (dark blue) and Burnt Umber (light blue), Raw Umber (yellow), Sepia (greenish blue) and Vandyke Brown (Brown). As one can see Sepia and Burnt Umber is most like the graph from "The musicband".

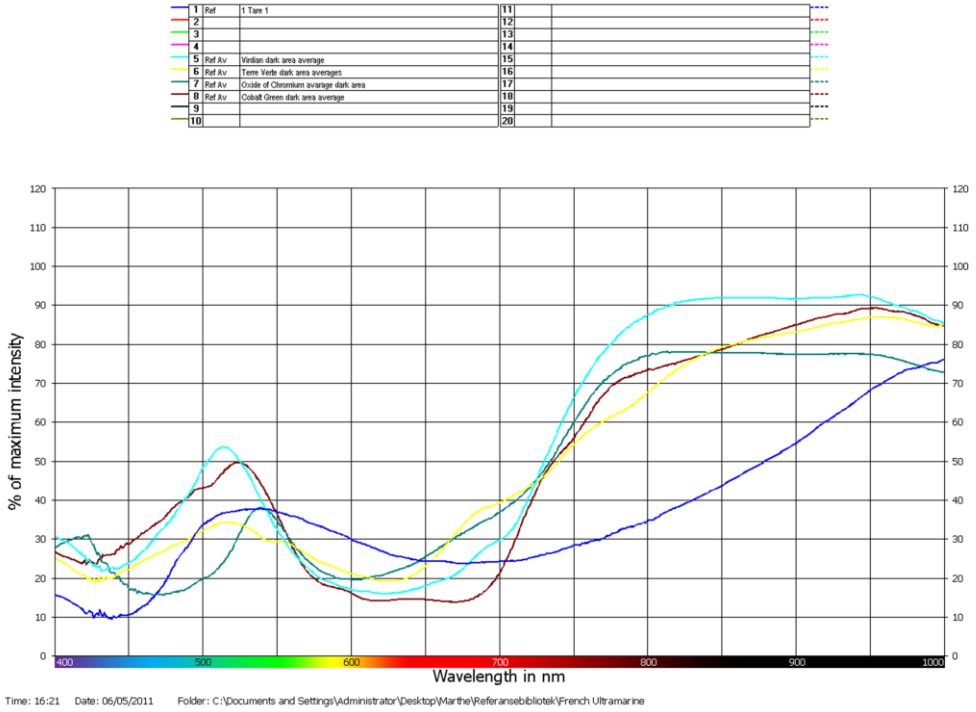

Figure 17: "Tare 1" (dark blue) and Cobalt Green (brown), Oxide of Chromium (greenish blue), Viridian (light blue), and Terre Verte (yellow). As one can see the graph does not have a strong resemblance to any of the references

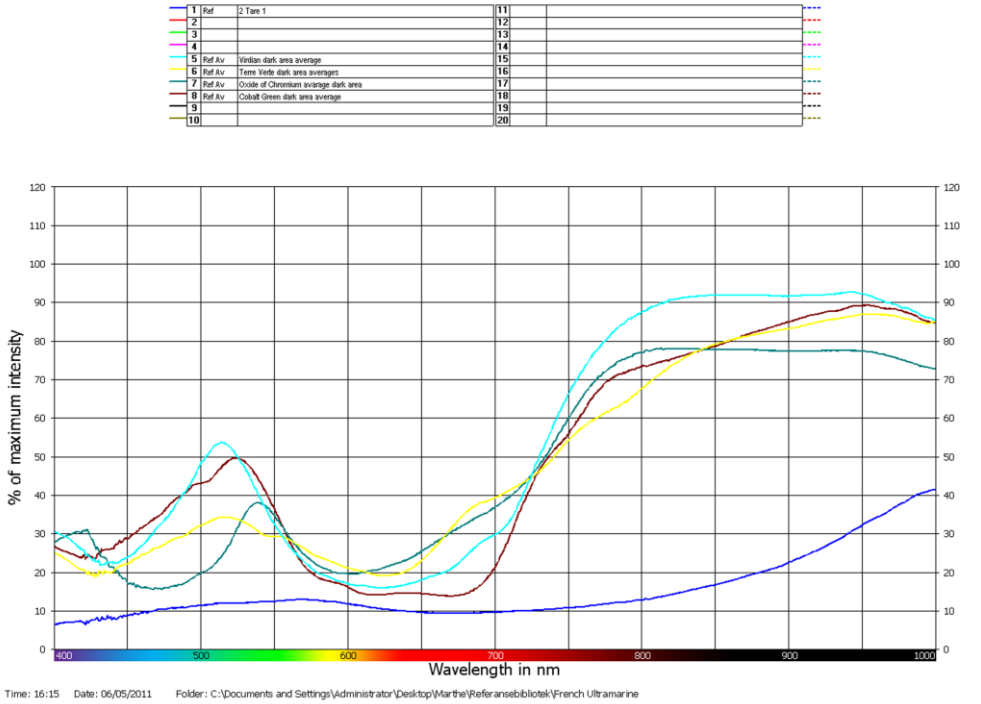

Figure 18: "Tare 2" (dark blue) and Cobalt Green (brown), Oxide of Chromium (greenish blue), Terre Verte (yellow) and Viridian (light blue). As one can see none of the references matches "Tare 2" well.

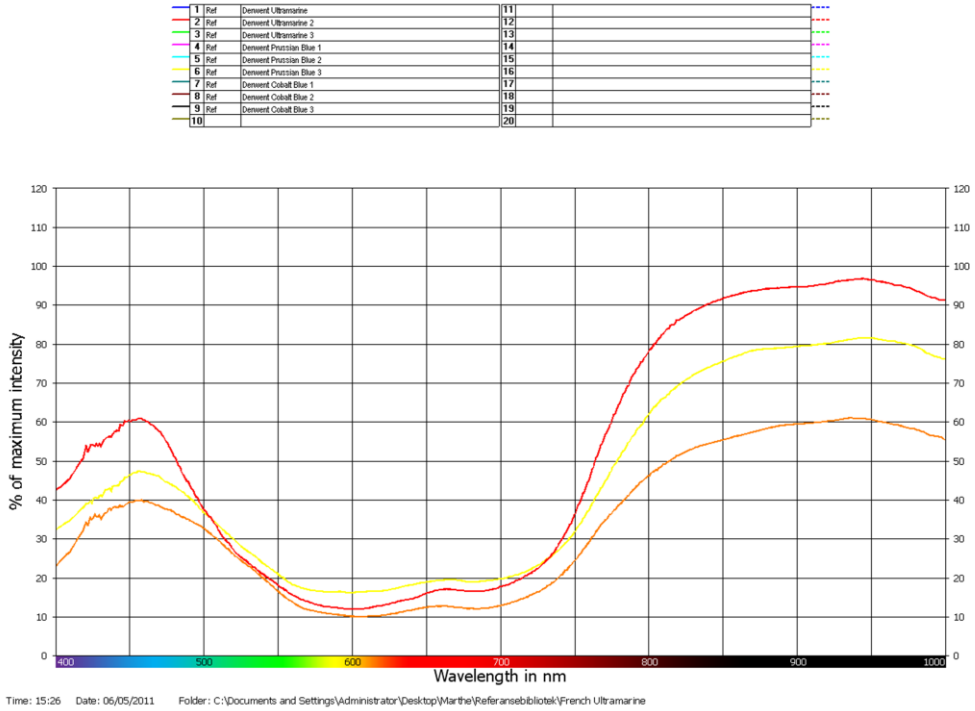

Figure 19: The blue Derwent Studio colors. Cobalt Blue (orange), Prussian Blue (yellow), and Ultramarine (red).

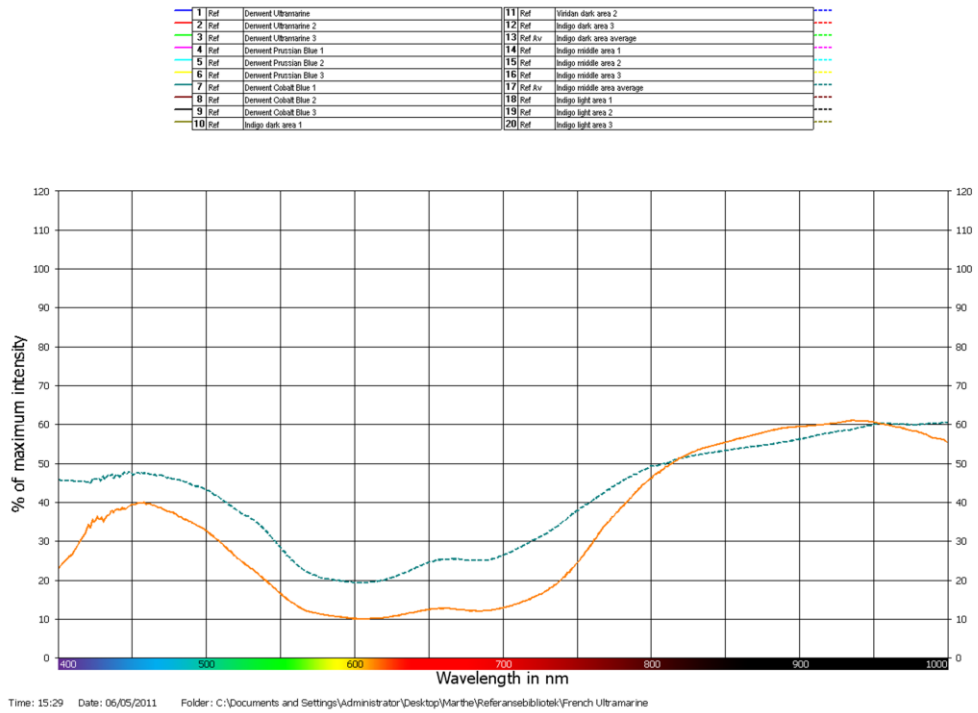

Figure 20: Indigo (dotted blue line) and the Derwent Studio's Cobalt Blue.

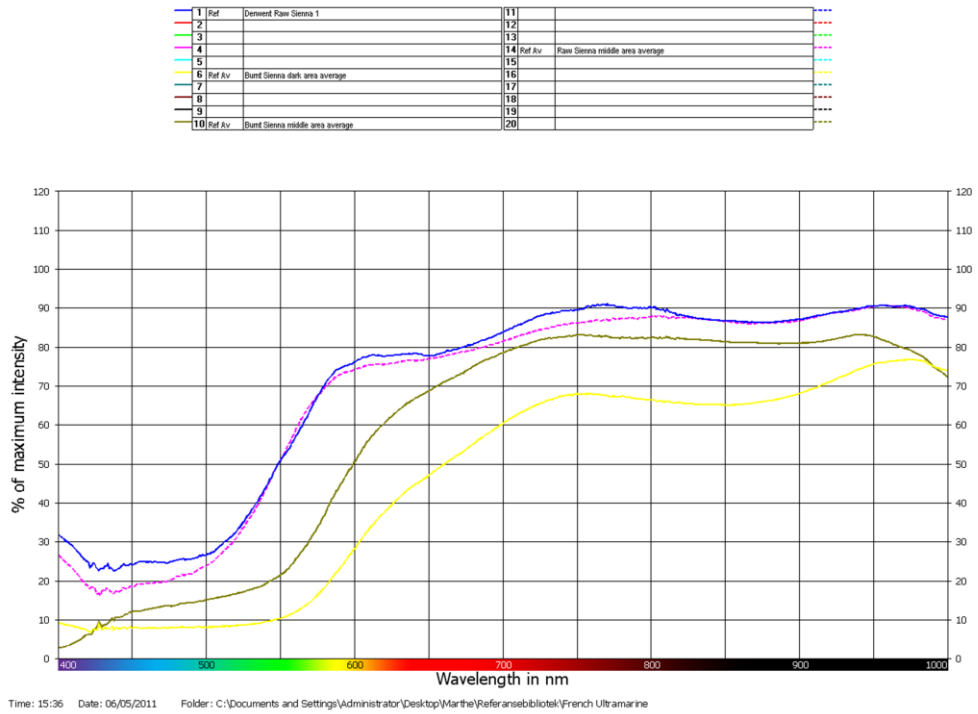

Figure 21: A graph from Derwent Studio's Raw Sienna (blue) and one graph form from Raw Sienna (dotted pink), two from Burnt Sienna (green and yellow).

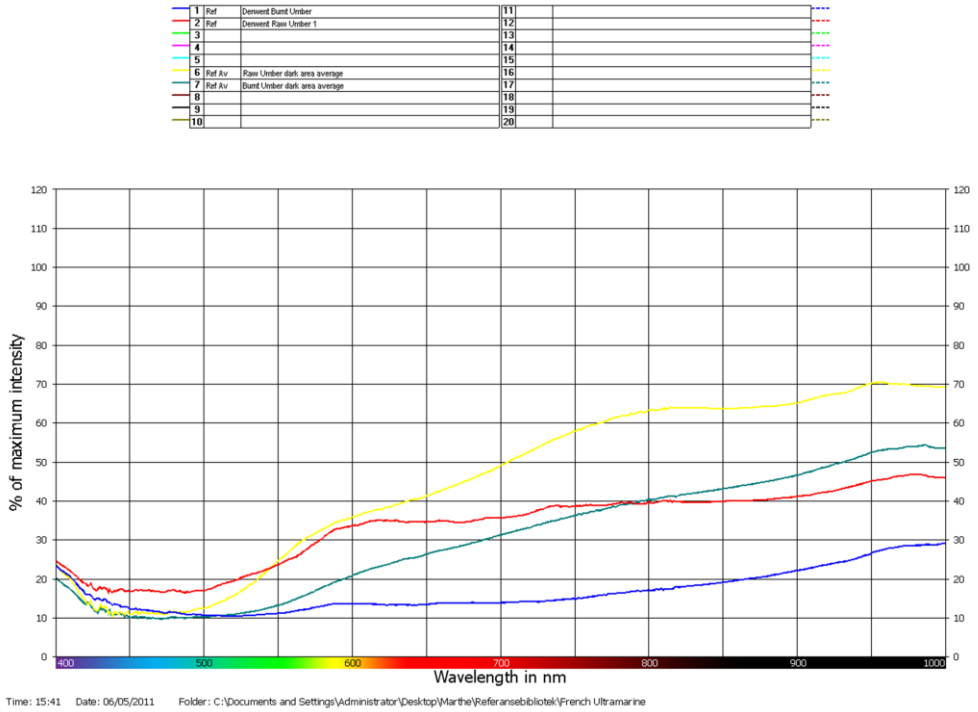

Figure 22: Graphs from Derwent Studio's Burnt Umber (blue) and Raw Umber (red) compared to the references Burnt Umber (greenish blue) and Raw Umber (yellow).

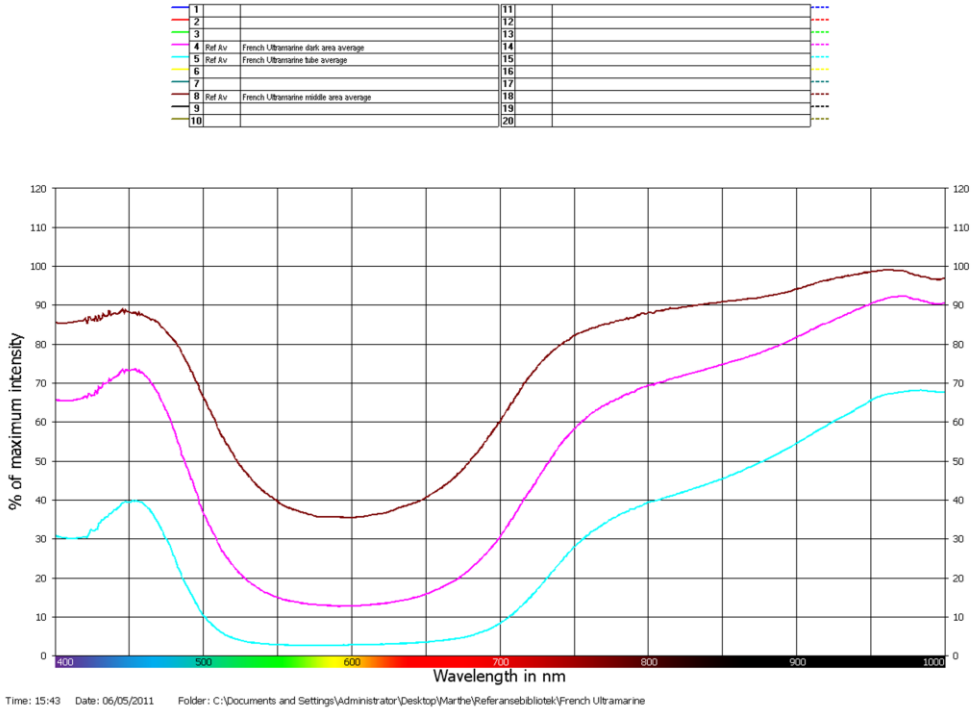

Figure 23: French Ultramarine tube color (light blue) and the reference French Ultramarine (brown and purple).

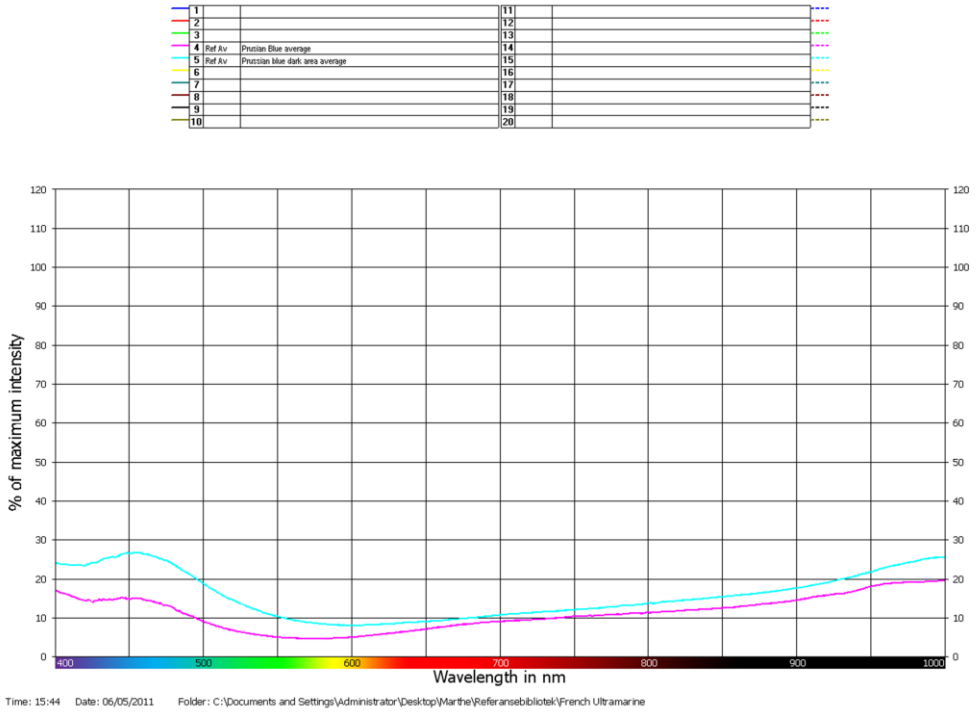

Figure 24: The Prussian Blue tube color (purple) and the reference Prussian Blue (light blue).

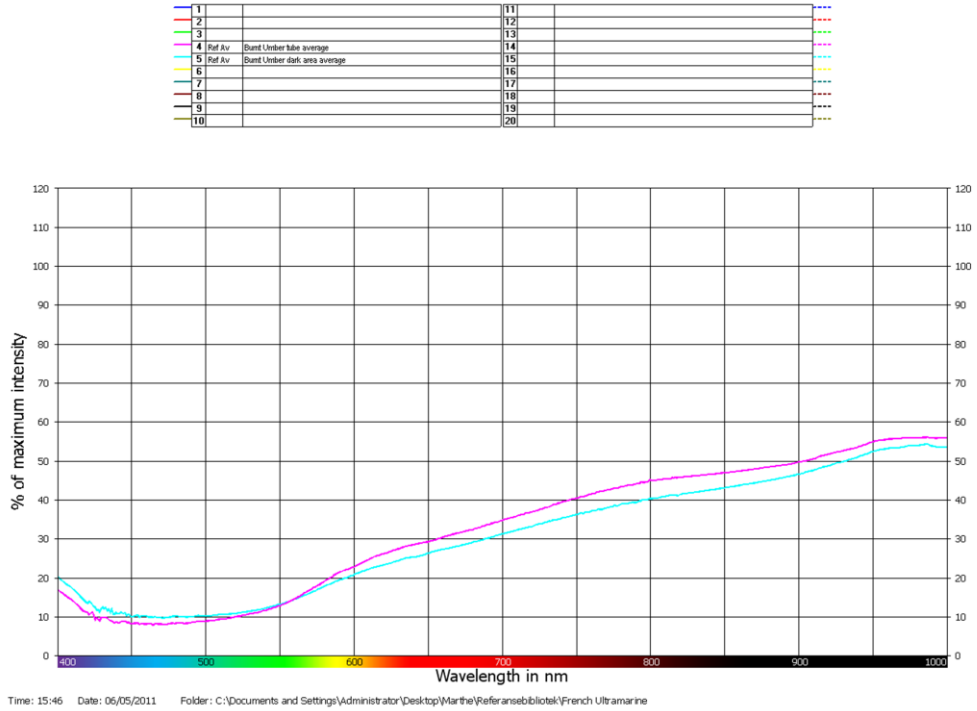

Figure 25: The Burnt Umber tube color (purple) and the reference Burnt Umber (light blue).

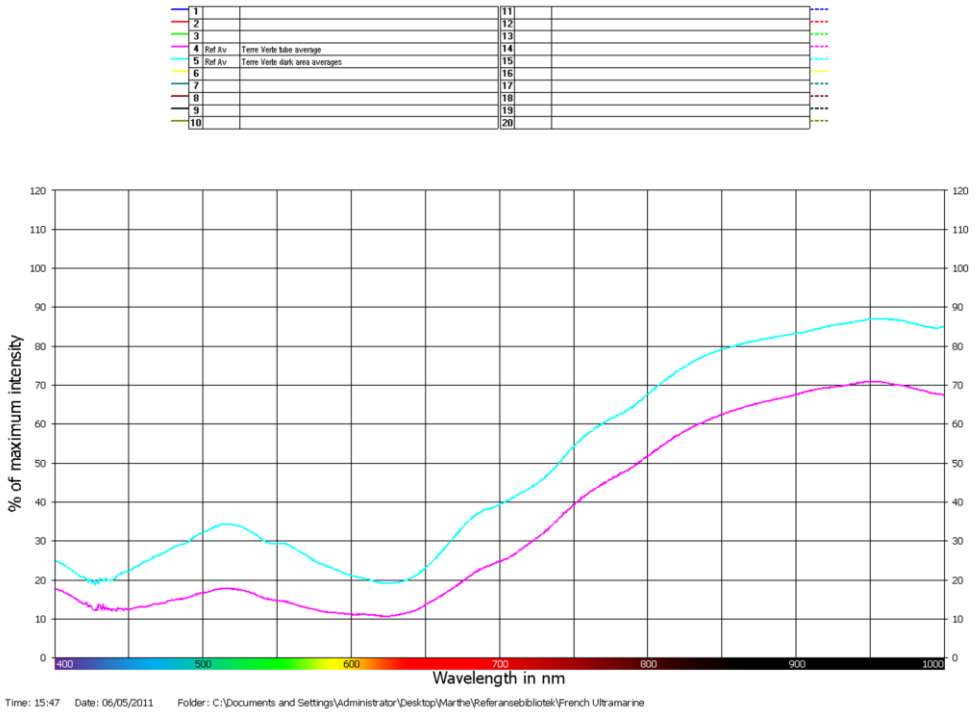

Figure 26: The Terre Verte tube color (purple) and the reference Terre Verte (light blue).

Appendix 5.UV-spectra

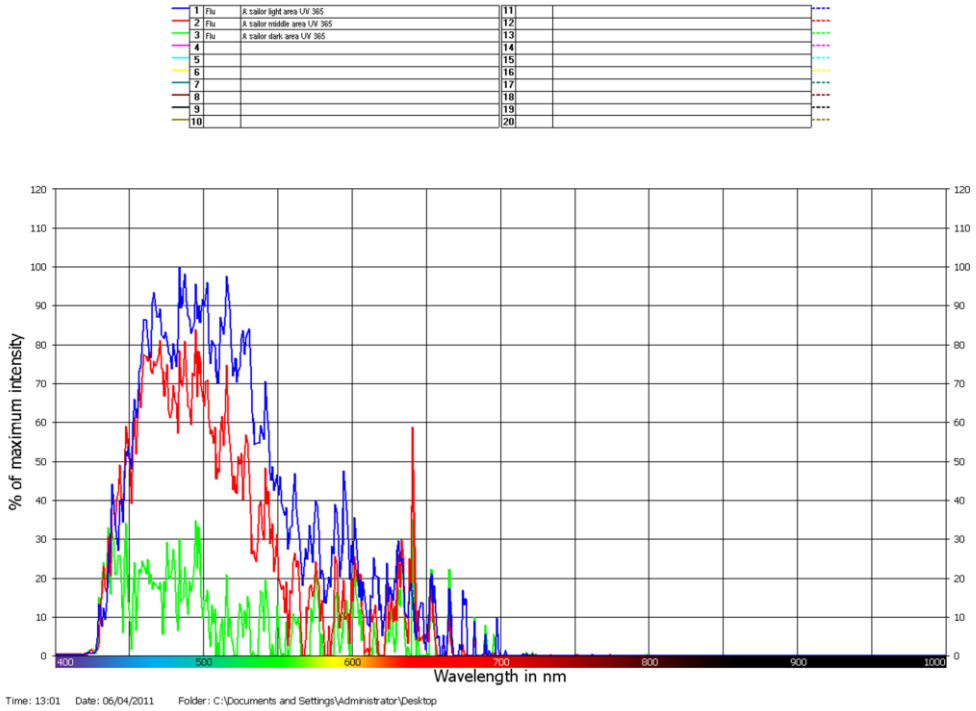

Figure 27: "A sailor", UV-365.

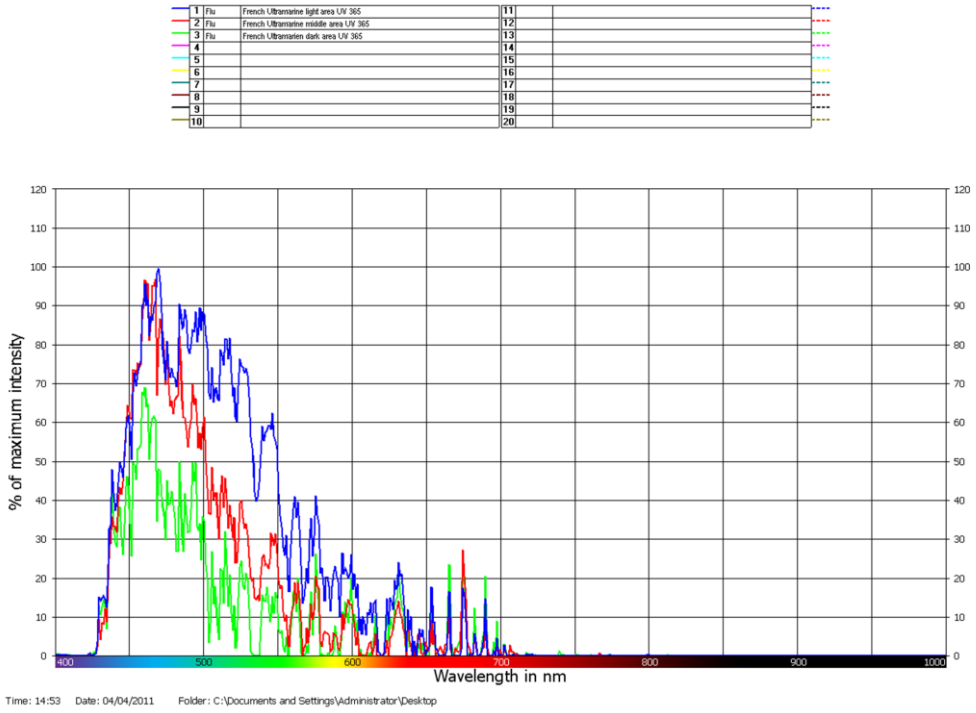

Figure 28: French Ultramarine, UV-365.

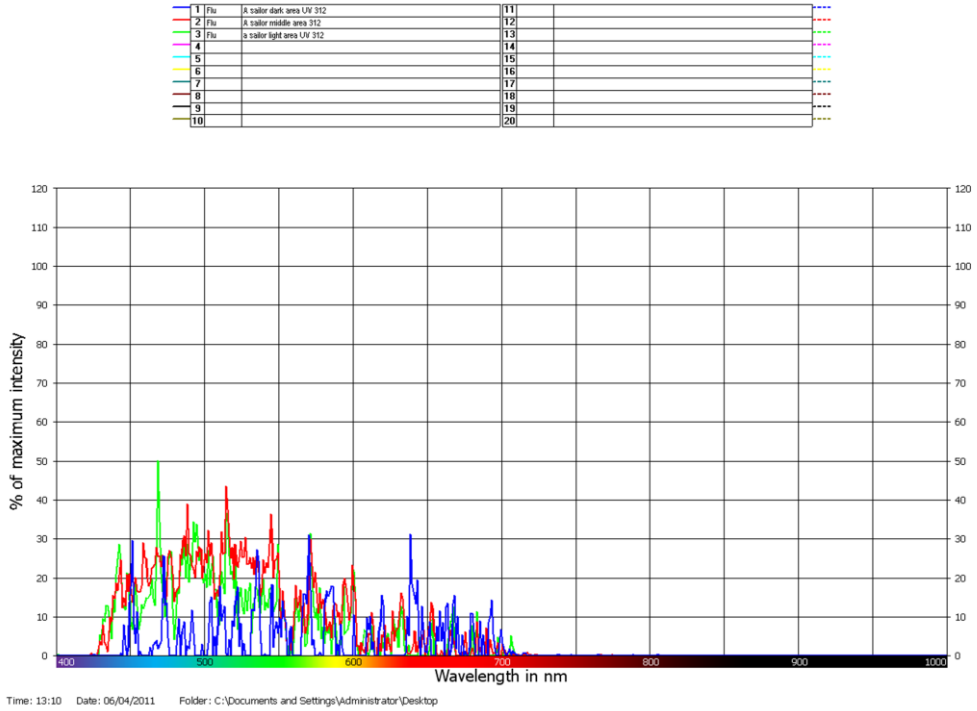

Figure 29: "A sailor", UV-312.

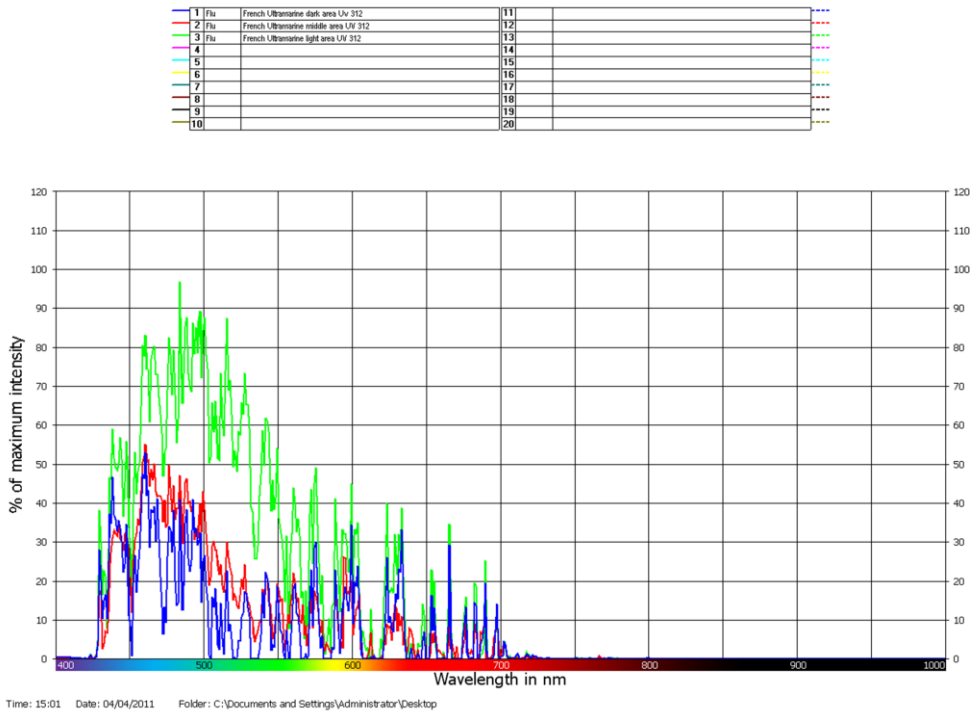

Figure 30: French Ultramarine, UV-312.

Appendix 6. Spot (fluorescence)

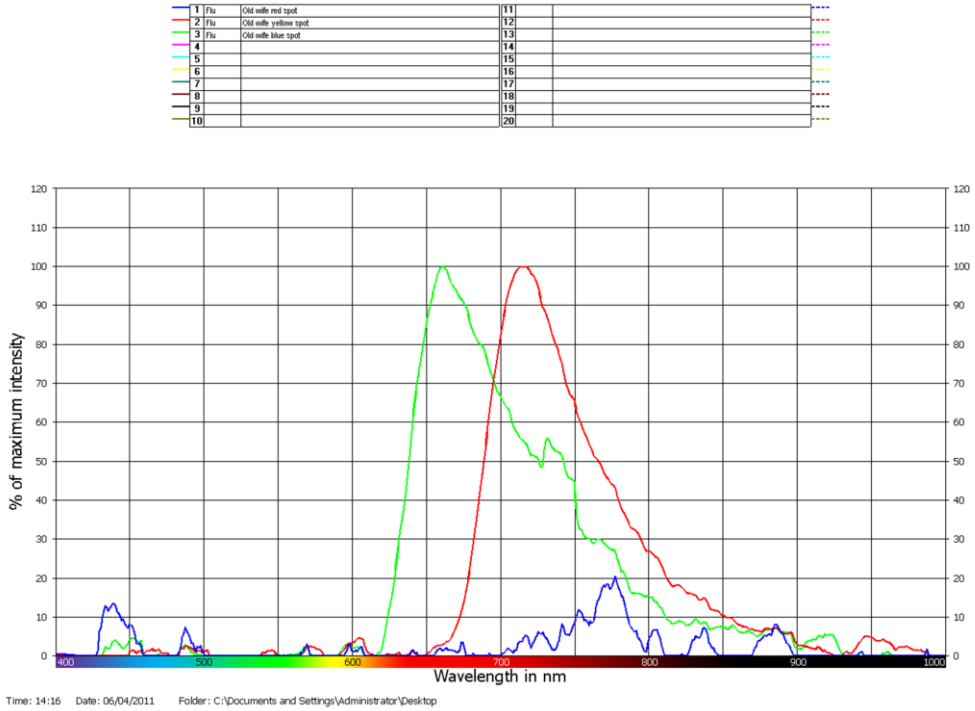

Figure 31: "Old wife". Red spot (blue), yellow spot (red), blue spot (green).

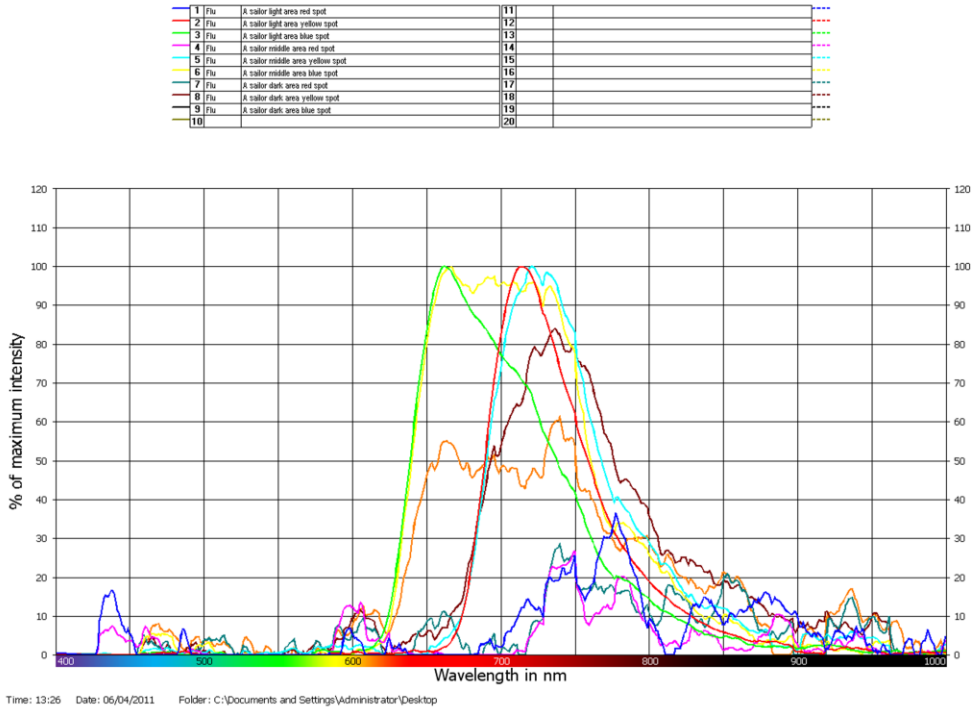

Figure 32: "A sailor". Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown) and blue spots (green, yellow and orange).

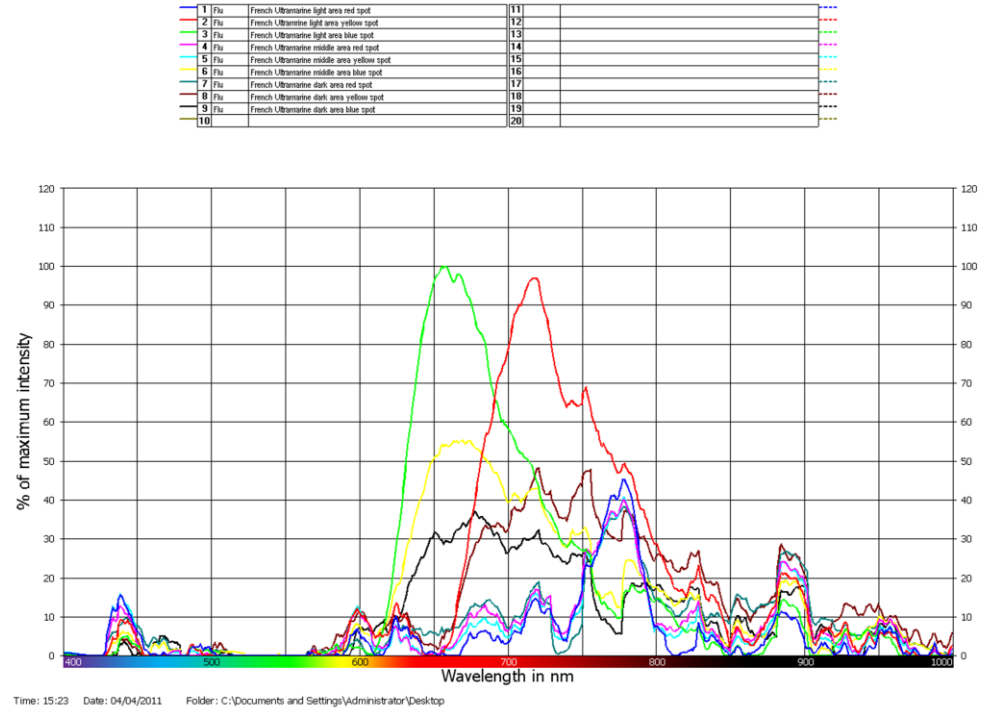

Figure 33: French Ultramarine. Red spots (dark blue, purple and greenish blue), yellow (red, light blue and brown) and blue spots (green, yellow and black).

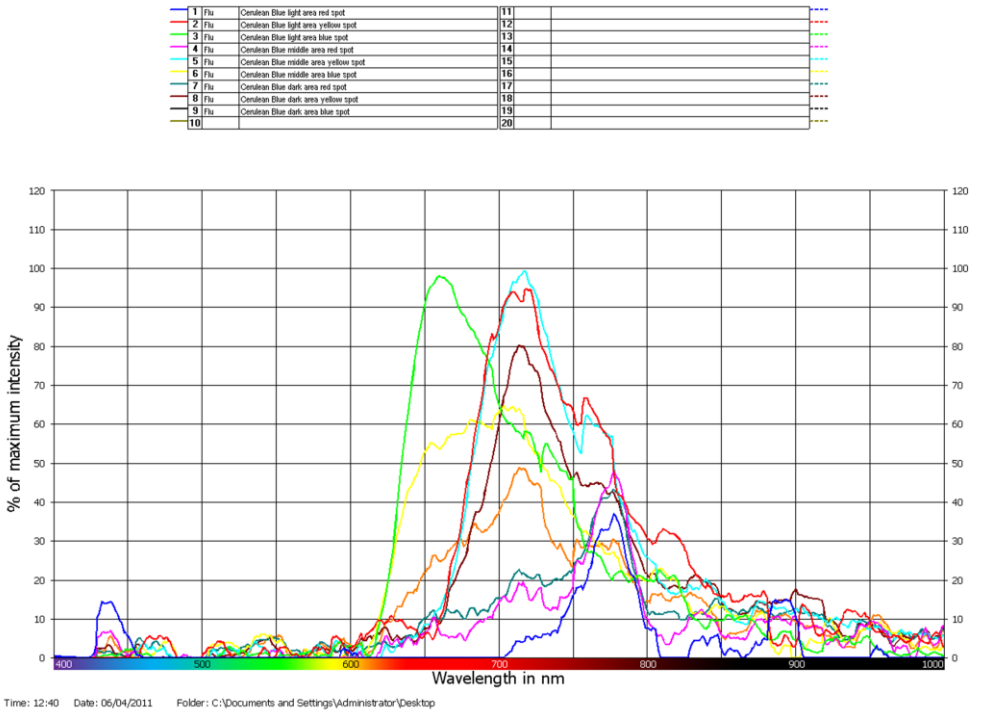

Figure 34: Cerulean Blue. Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown) and blue spots (green, yellow and orange).

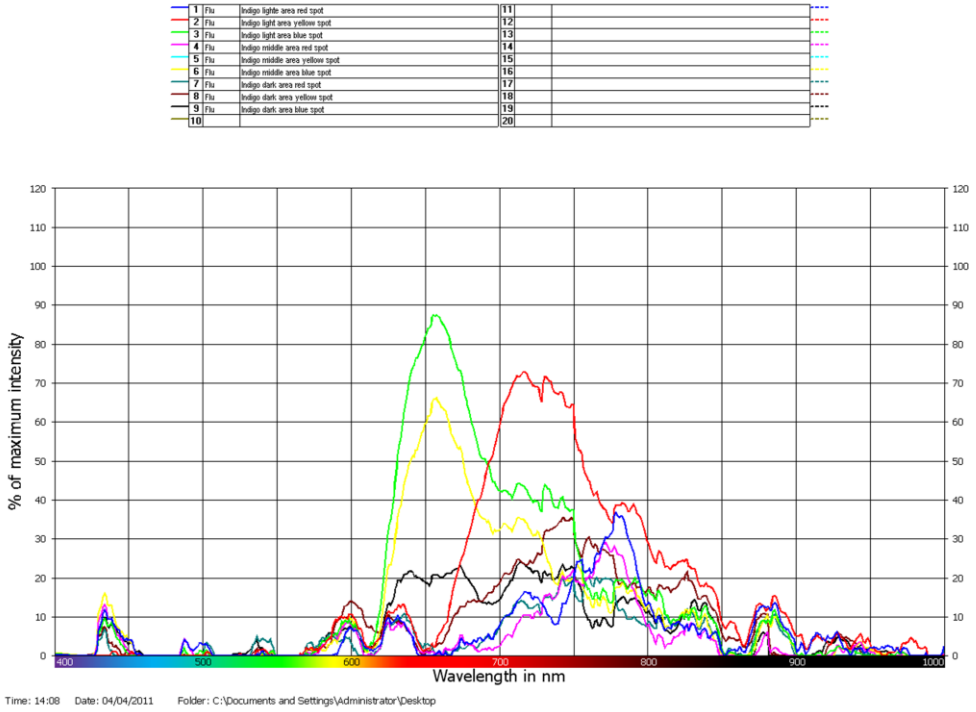

Figure 35: Indigo. Red spots (dark blue, purple and greenish blue), yellow spot (red, light blue and brown), and blue spots (green, yellow and black).

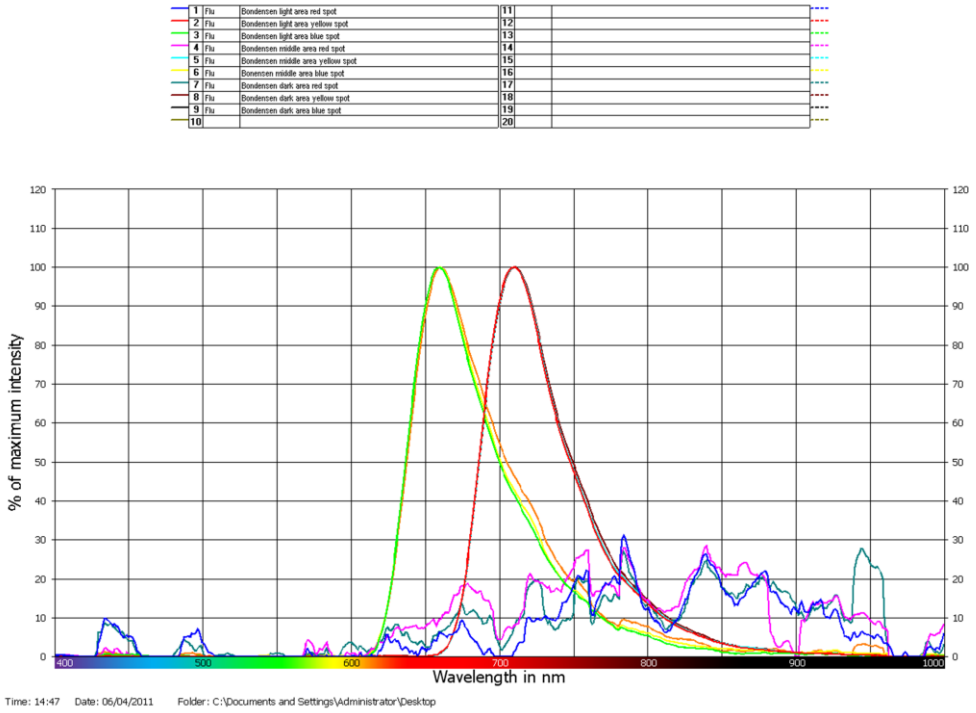

Figure 36: "Bondensen". Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and orange).

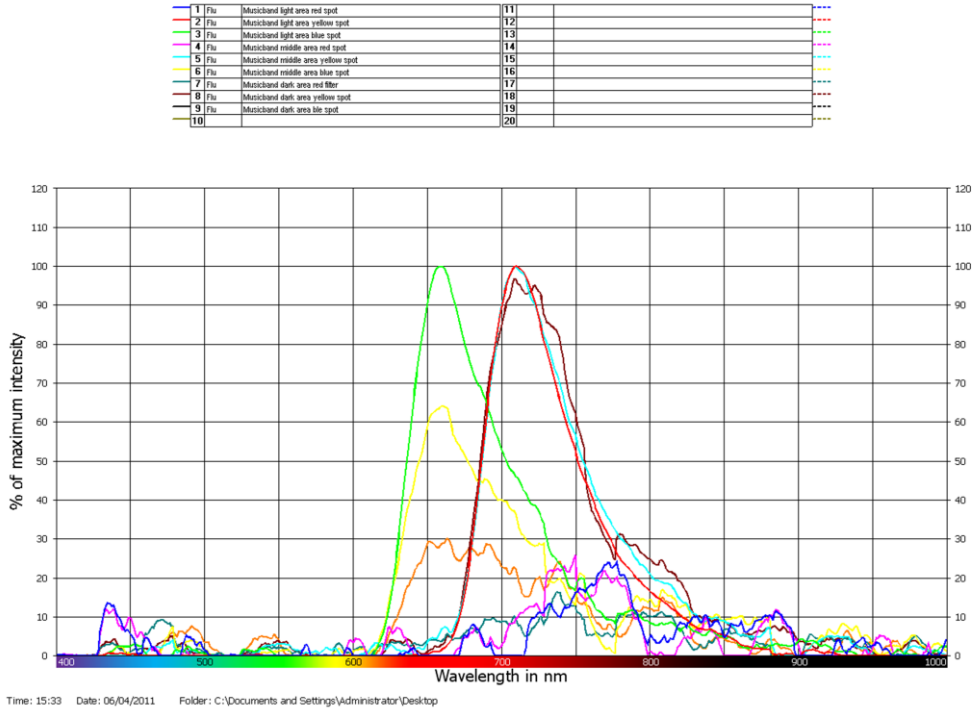

Figure 37: "The musicband". Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and orange).

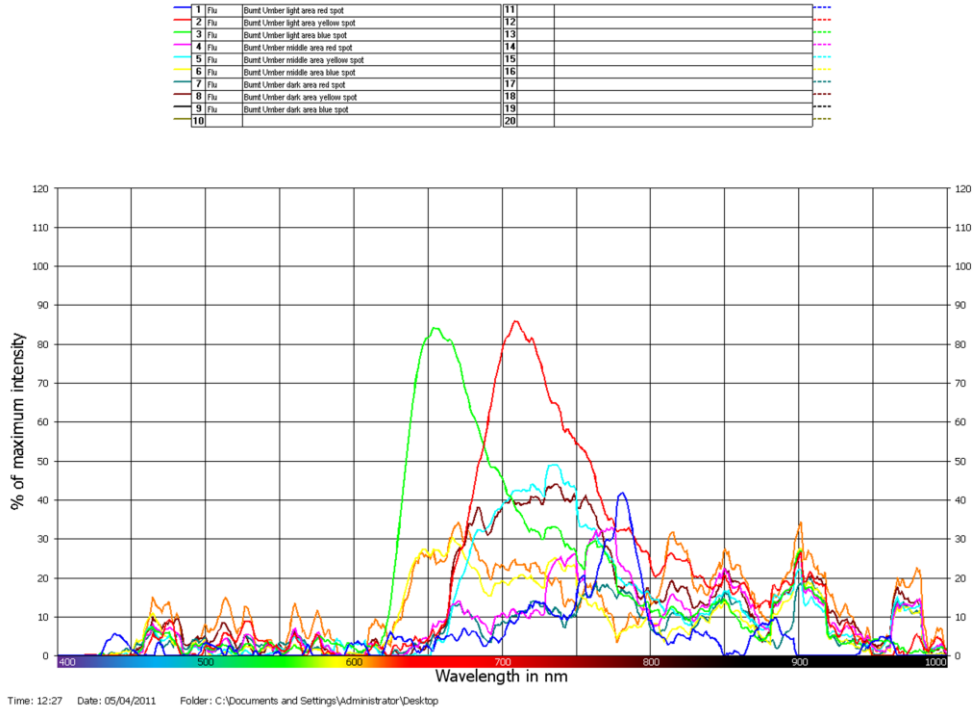

Figure 38: Burnt Umber. Red spots (dark blue, purple nad greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and orange).

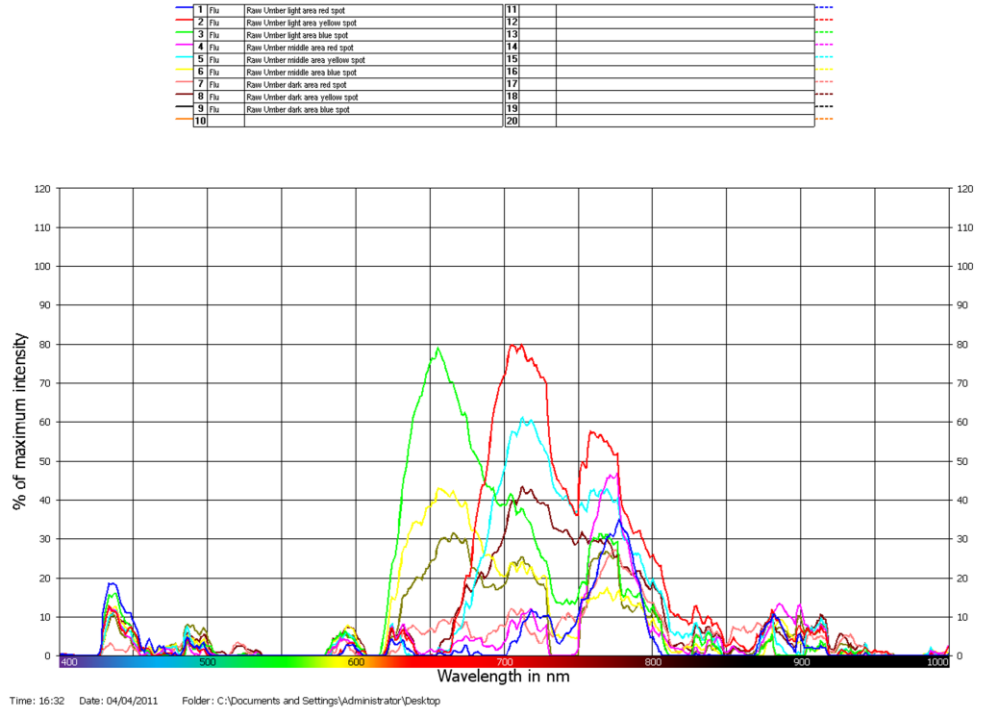

Figure 39: Raw Umber. Red spots (dark blue, purple and pink), yellow spot (red, light blue and brown) and blue spots (green, yellow and dark green).

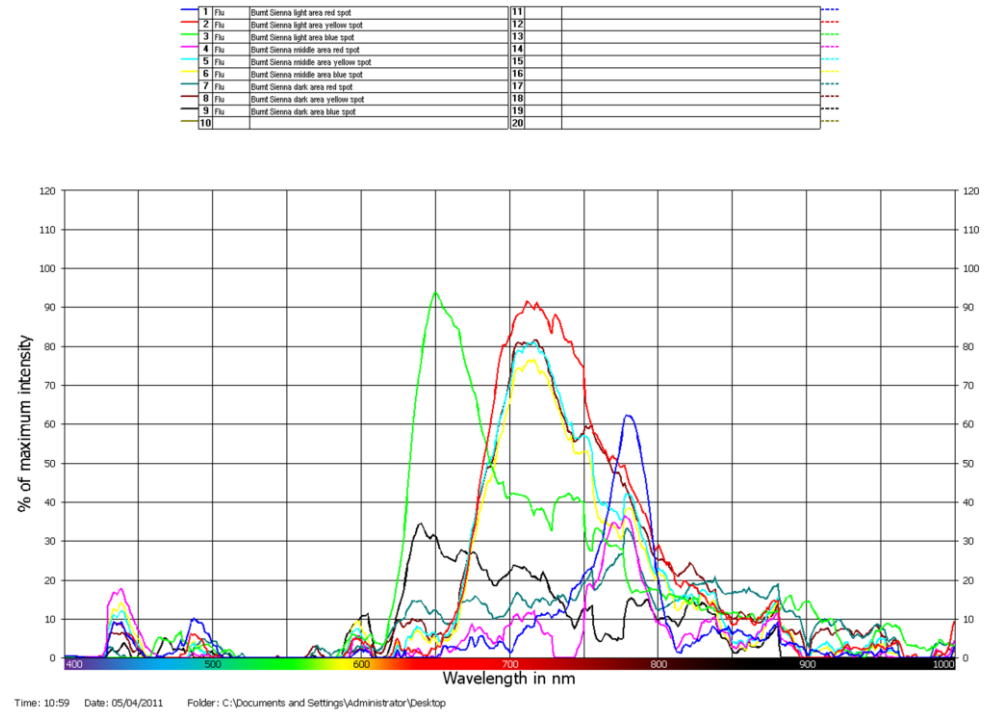

Figure 40: Burnt Sienna. Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and black).

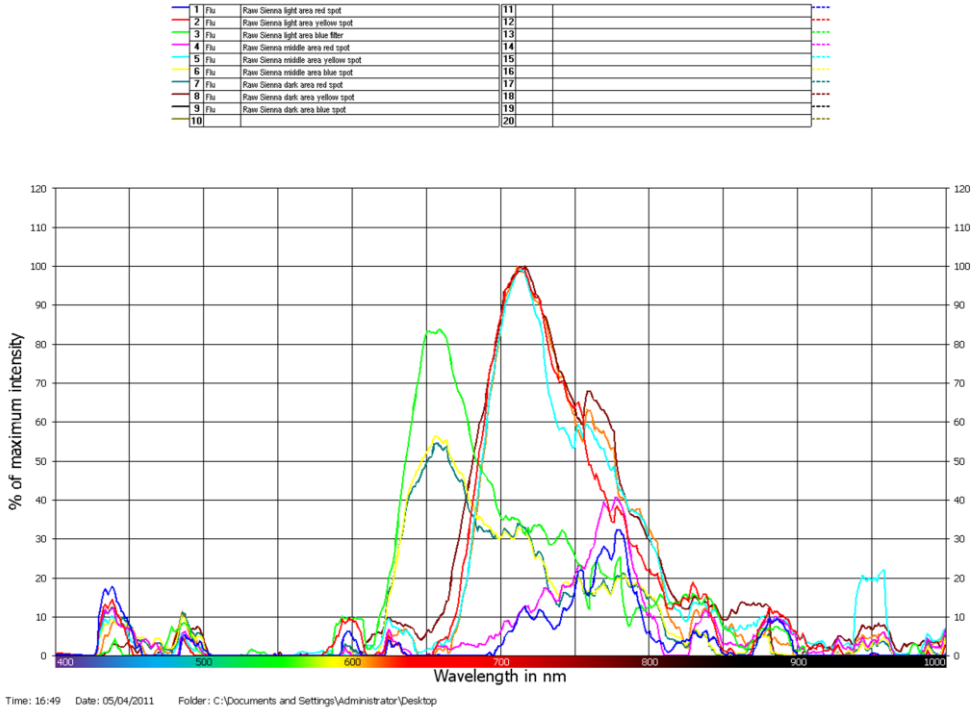

Figure 41: Raw Sienna. Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and dark green).

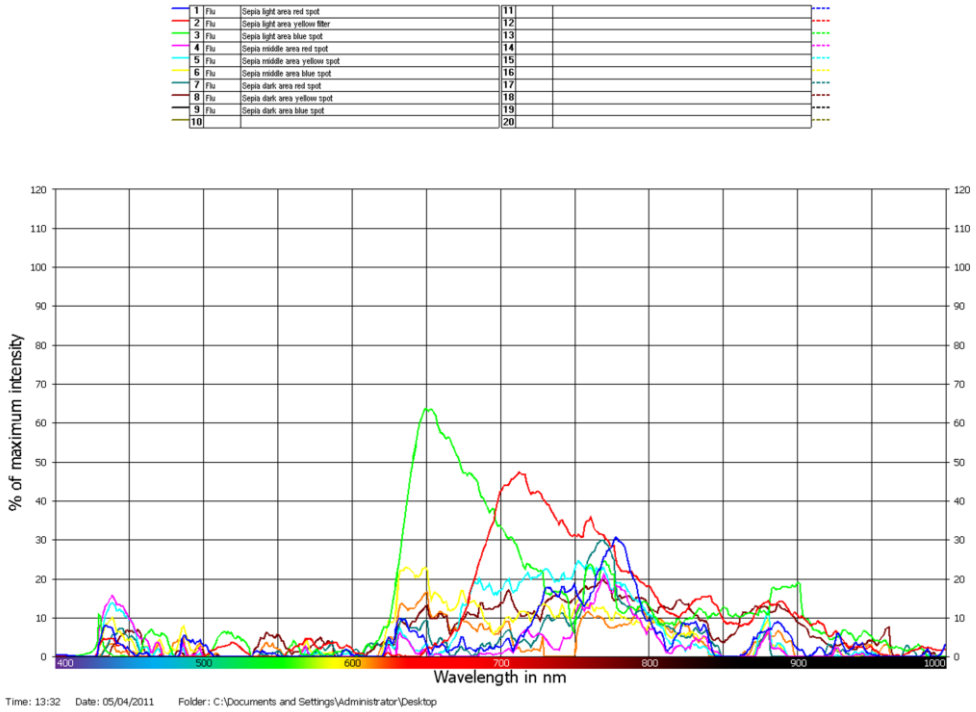

Figure 42: Sepia. Red spots (blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green yellow and orange).

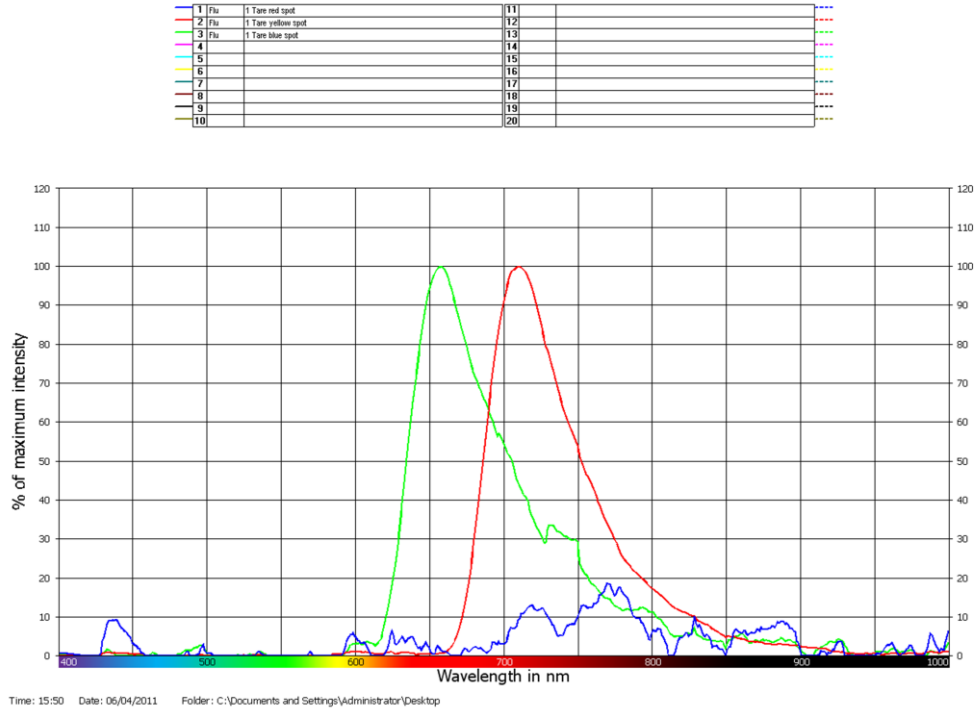

Figure 43:" Tare 1". Red spot (blue), yellow spot (red), and blue spot (green).

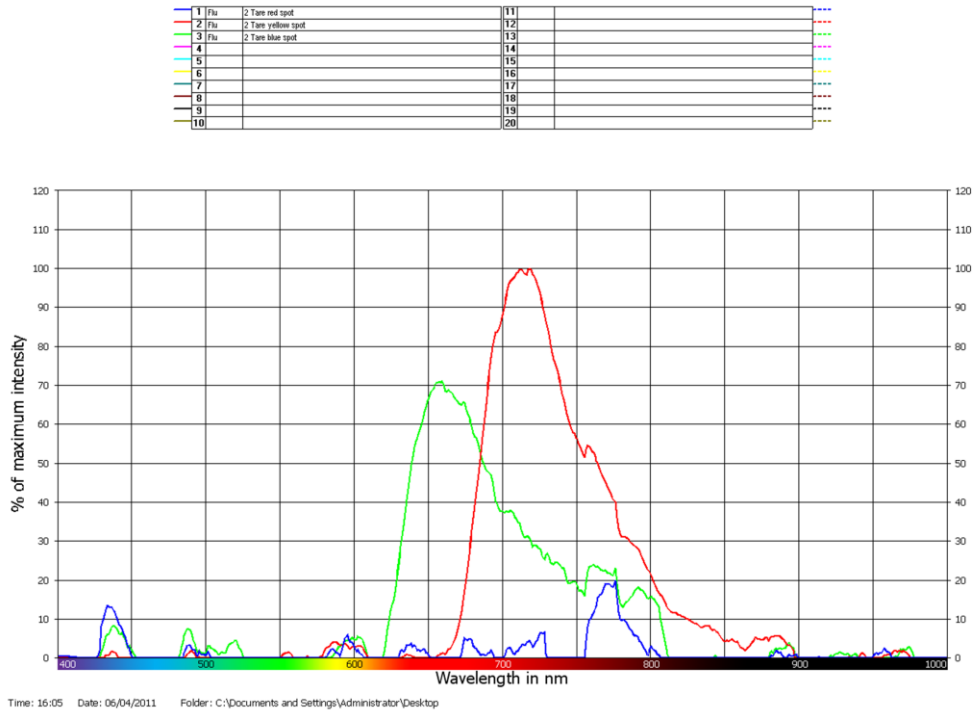

Figure 44: "Tare 2". Red spot (blue), yellow spot (red), and blue spot (grren).

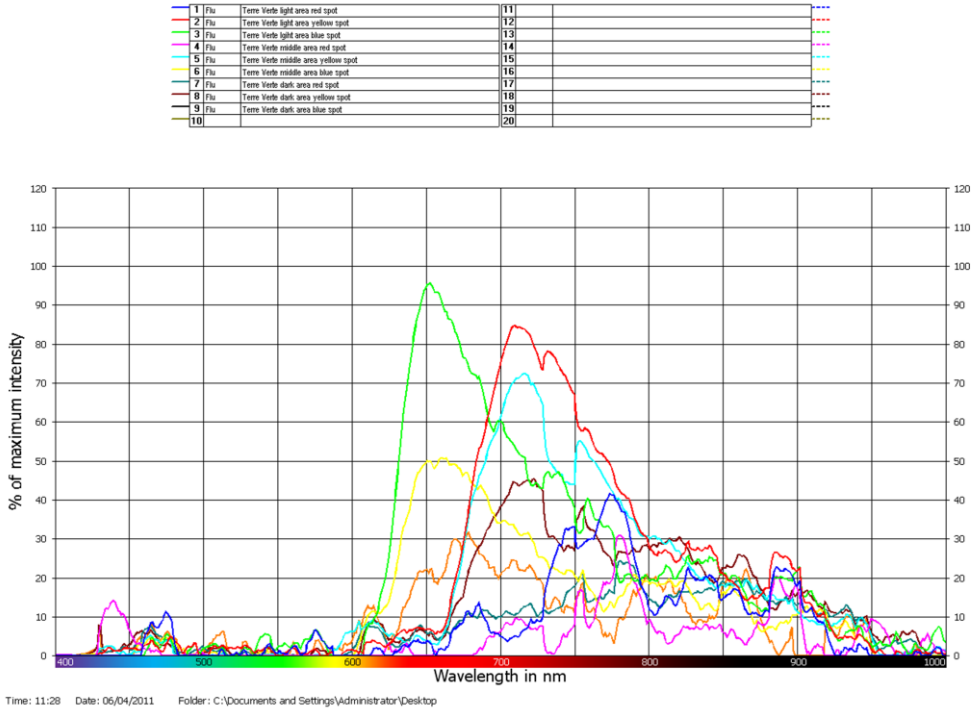

Figure 45: Terre Verte. Red spots (dark blue, purple and greenish blue), yellow spot (red, light blue and brown), and blue spot (green, yellow and orange).

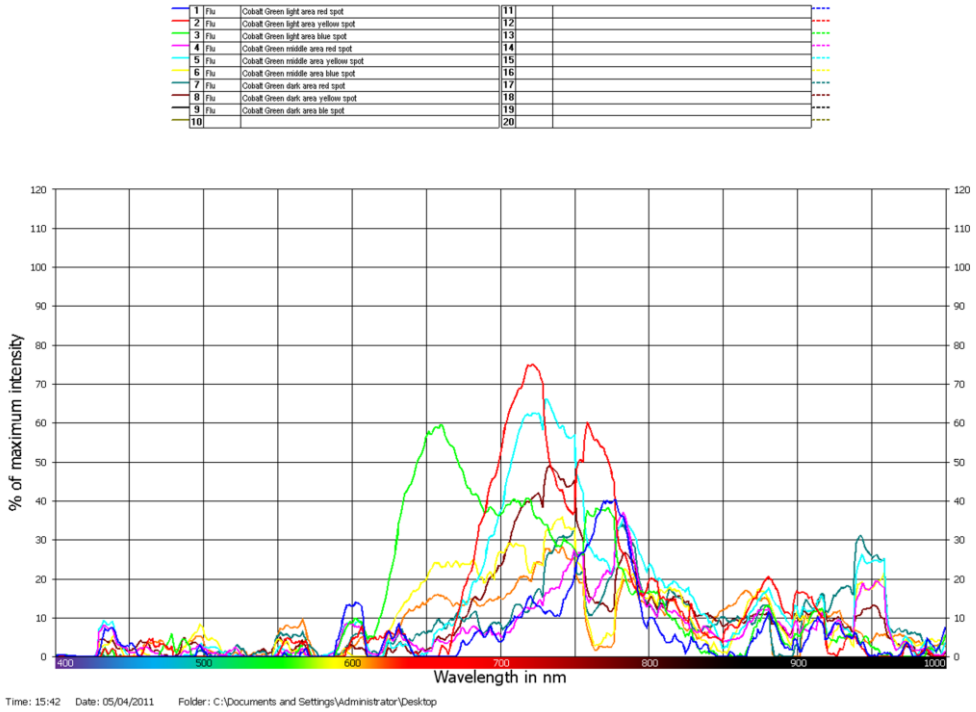

Figure 46: Cobalt Green. Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and orange).

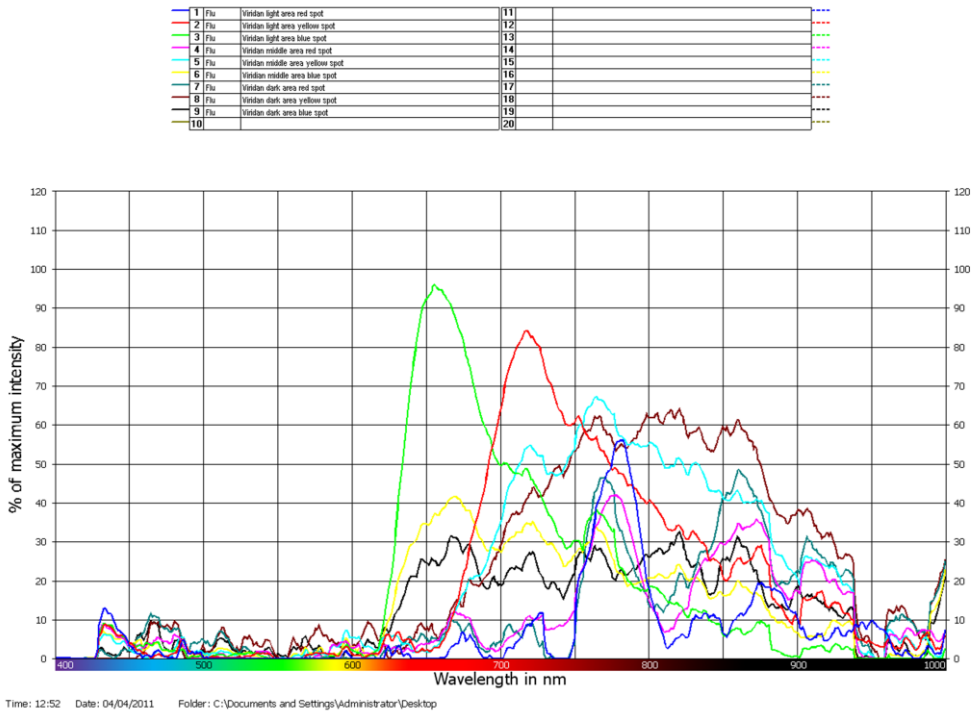

Figure 47: Viridian. Red spots (dark blue, purple and greenish blue), yellow spots (red, light blue and brown), and blue spots (green, yellow and black).

Appendix 7: SEM results

"Old wife"

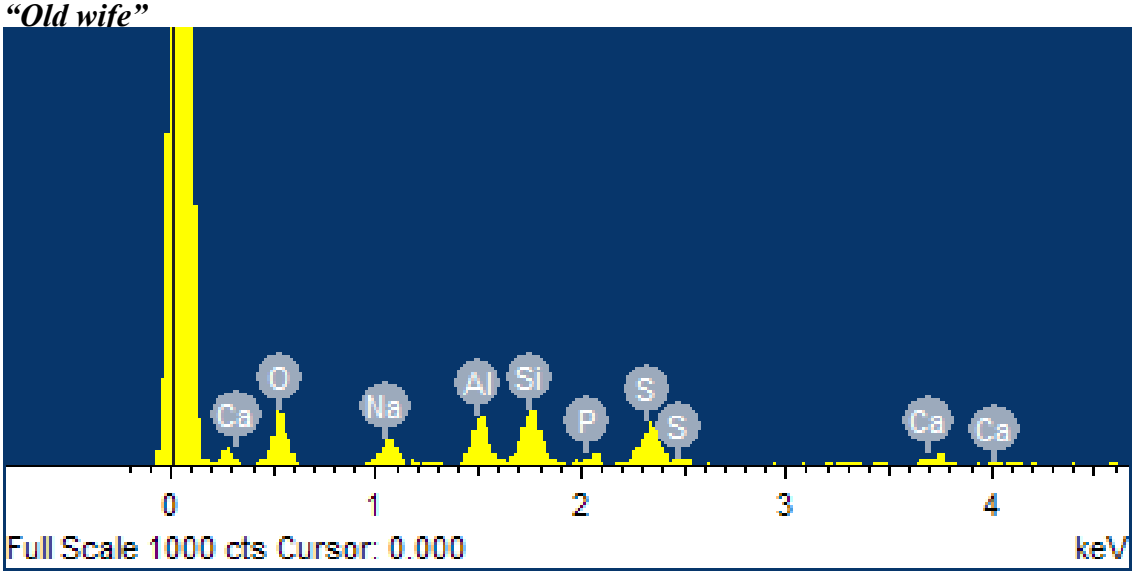

Figure 48: The SEM results from "Old wife". Soda, aluminium and sulphur indicate that this is Ultramarine.

"A sailor"

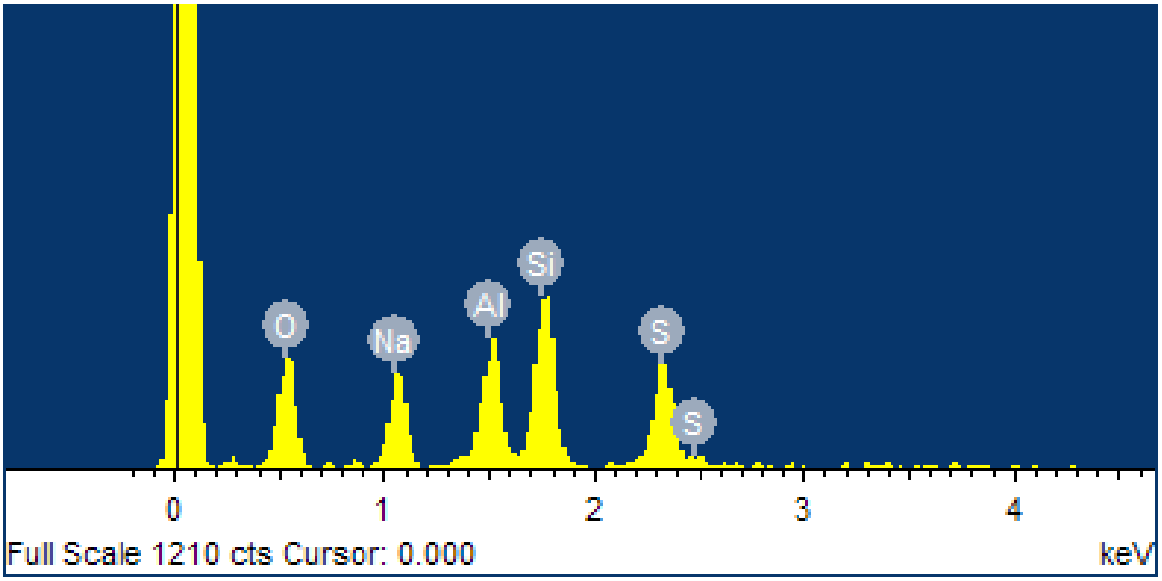

Figure 49: "A sailor". The SEM results show elements that are used in Ultramarine.

"Bondensen"

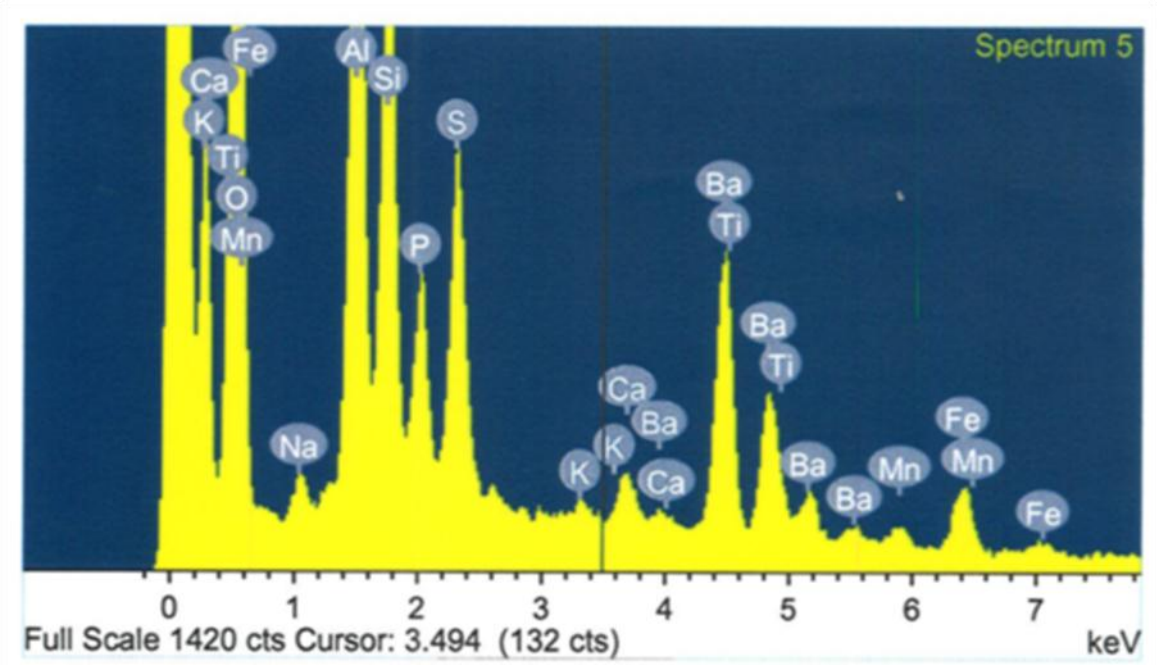

Figure 50: The SEM results from "Bondensen". Among other elements the manganese indicates an earth color

"The musicband"

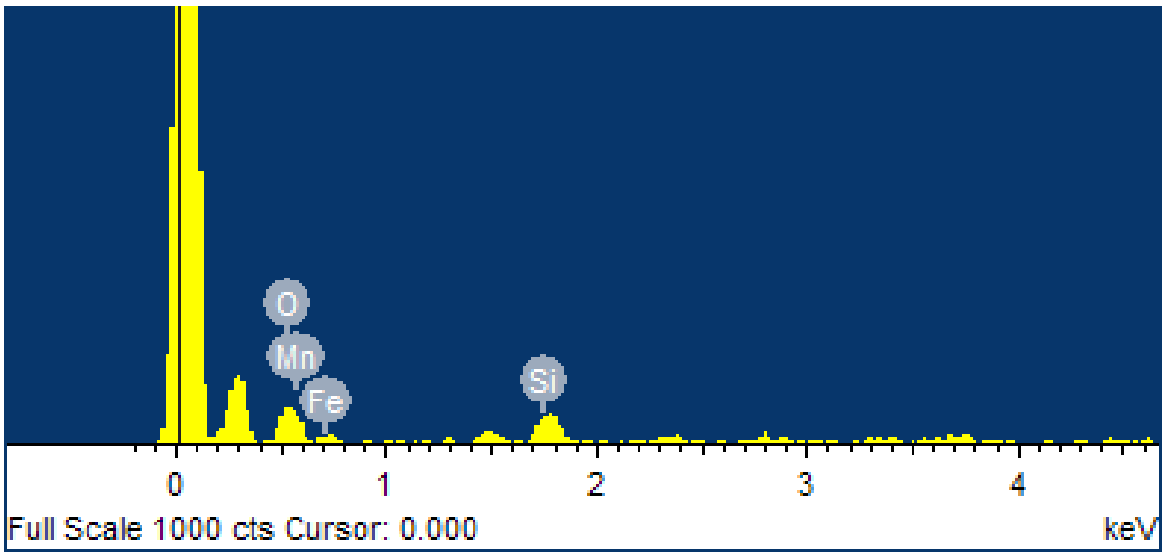

Figure 51: The SEM results from "The musicband". The manganese indicates that it is an earth color.

"Tare 1" (light green)

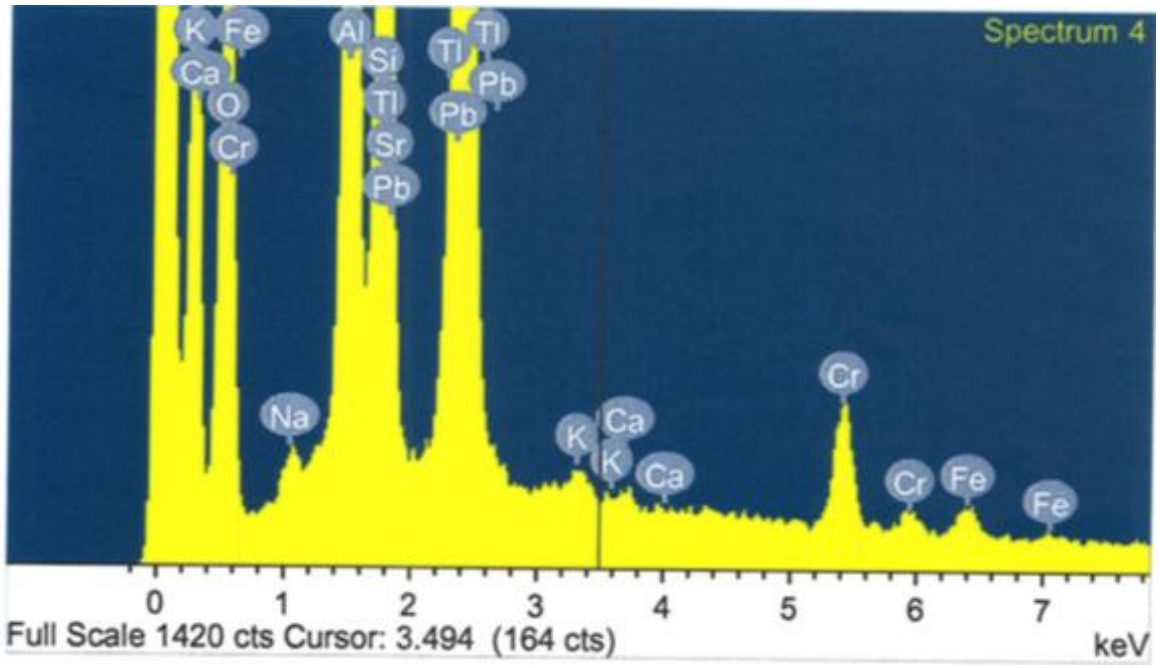

Figure 52: The SEM results from "Tare 1" . The lead and chrome indicates Chrome Yellow. An the blue color is probably Prussian Blue.

"Tare 2" (dark green)

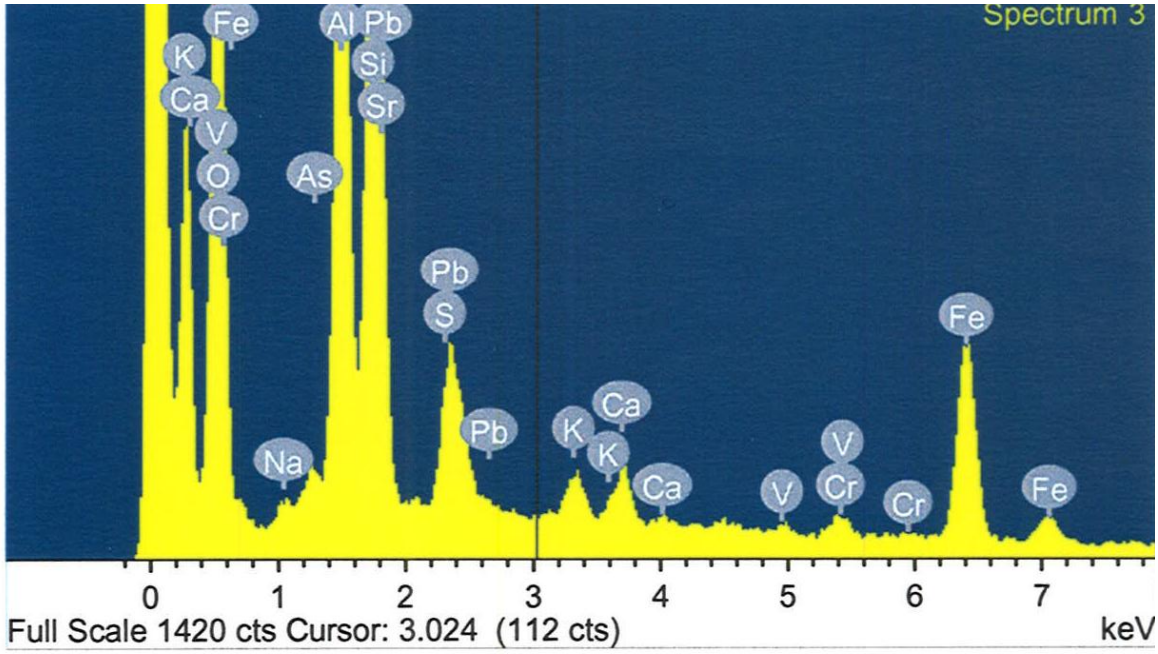

Figure 53: The lead and chrome indicates Chrome Yellow. The blue color might come from Prussian Blue or Ultramarine.