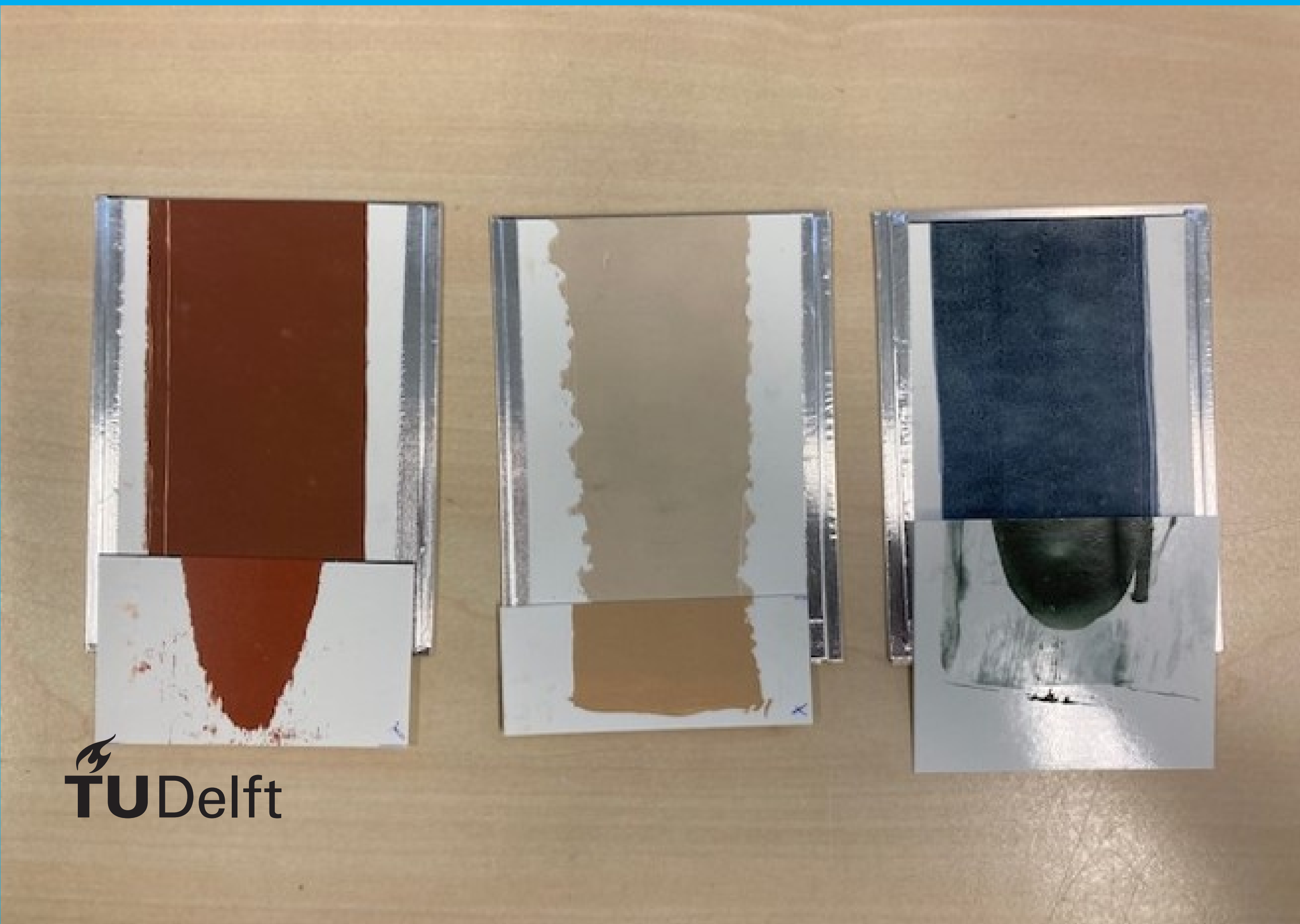
Colour changes in *Girl with a Pearl Earring*

L.C.A. Oude Luttikhuis



TU Delft

Colour changes in Girl with a Pearl Earring

by

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Cover picture taken by Helen Veringmeier-Heemskerk from AkzoNobel. The small bottom samples show the reconstruction of three paint colours from *Girl with a Pearl Earring*. The larger top samples show the the colour change in those paints after 456 hours of artificial aging.

TU Delft

Preface

With the completion of this project, my time at the TU Delft comes to an end. My journey here began already when I was in primary school. A trip towards the university helped spiking my interest in going here someday. And I did. After a short stay at Architecture, I finished a bachelor in Applied Physics. For a masters, I picked Materials Science and Engineering, which was unfortunately disturbed by the covid lockdowns. Luckily, there where also many highlights during my time here like my board year at Punch, and all activities there, doing a geophysics minor in Utrecht, and playing Mario Kart (and some working) for a summer at TOPdesk. I improved myself not only on academic level, but I made sure to do so on other levels as well. This all would not have been possible without the help of many people. My board mates and girls from Cosmo. Iris for all long phone calls and Jurjen for always being down to earth. My parents for supporting me in my choices. And finally, André, who was there since the beginning of my time in Delft, for everything.

L.C.A. Oude Luttikhuis
Delft, March 2023

Contents

1 Introduction

1.1. About the Painting

The painting *Girl with a Pearl Earring* was made around 1665 by Johannes Vermeer (Delft, 1632-1675) and can be seen in figure 1.1. Vermeer made relatively few paintings [1]. This one is different from most of them [2, 3] since it is one of only two *tronies* (character studies) and shows a young woman in front of a flat, dark background [3]. In many of this paintings, Vermeer painted people who are standing in a typical Dutch house [1] in front of a light-coloured background. This was common in the 17th century Dutch tradition [4]. Due to the dark background in this painting the 3D effect is enhanced [3, 4]. In 1881 the painting was recognised as a Vermeer and sold for only two guilders [2, 4] and in 1903 it was donated to the Mauritshuis museum, where it still is exhibited and visited by people from all over the world [2]. When the painting was bought in 1903 it was in a *deplorable state of neglect* and therefore the painting was restored, which was also done in 1915, 1922, 1960 and 1994 [4]. Since the techniques for scientific research improved over the years, a technical re-examination was executed in 2018 during the project *The Girl in the Spotlight* [5].

Figure 1.1: The painting *Girl with a Pearl Earring* by Johannes Vermeer. Image obtained from [2].

1.2. The Girl in the Spotlight

Since the restoration in 1994, the painting has been in a stable state and does not need to be treated in the near future. In 2018, *The Girl in the Spotlight* project started in which the *Girl* underwent a technical examination. The possibilities for non-invasive research improved significantly over the years, making it possible to find out more about Vermeer's techniques and materials and the evolution of the painting [5]. The primary topics were the materials used in the background, the techniques Vermeer used and to document the current state of the painting. The main research questions were (literally obtained from [5]):

- What steps did Vermeer take to create the painting?
- What can we find out about layers beneath the surface?
- Which materials did Vermeer use and where did they come from?
- Which techniques did Vermeer use to create subtle optical effects?
- What did the painting look like originally, and how has it changed?
- What is the chemical and physical condition of the painting?

To make the visitors still be able to see the painting, the examination was visible to the public. This analysis lead to a broader understanding of the painting, which was published in seven articles about the underlayers [6], pigment distribution [7], topography [8], secondary reaction products [9], skin [10], ultramarine [11] and the background [3]. However, despite the knowledge gained, not all research questions were answered. Mainly, it is not clear how the painting looked like when Vermeer finished it and how it has been degraded over time [12].

1.3. Motivation

A lot of research has been done on *Girl with a Pearl Earring* already. This, however, was mostly research on the current or original state of the painting. What has not been done is investigating how the painting changed over time and how that affected the appearance of the painting. New computational methods provide opportunities to simulate behaviour of colour change in paintings. The combination of art history and computational methods is unique and not utilised yet. This has also never been done before on other paintings, despite the interesting possibilities it offers. Therefore the goal of this research is to combine both fields and to create a simulation of the colour change in *Girl with a Pearl Earring* over time. To do so, reconstructed samples of the original paint will be artificially aged using UV light, creating samples with different stages of the colour change. BRDF (bidirectional reflectance distribution function) measurements can then be used to create a digital simulation of the colour change of the painting. The lessons learned from this research can be used in upcoming research on *Girl with a Pearl Earring* and on other paintings. Furthermore, the data which will be acquired will be presented at the Mauritshuis to give the public the opportunity to learn more about this subject.

1.4. Report Overview

This report will focus on reproducing the degradation of the colours on *Girl with a Pearl Earring* and to digitally reconstruct the look of how the painting has changed over time. This can be divided in the following sub questions, which will all be expanded in a separate chapter:

- **What is the build up of a 17th century painting and what materials are used?**
  Chapter 2 will describe the layers in the painting and the materials they are made of. All used paints are also described in detail. Furthermore, the optics of paint layers are explained and the basics of colour quantification is explained.
- **What types of degradation mechanisms can occur in paintings and which are relevant for this painting?**
  There are several ways in which paintings can degrade, for example fading of lakes and lead soap formation. These phenomena, and more, are explained in chapter 3. Furthermore, the historical context and effects on perception of colour changes are described as well.

- **How can colour degradation be measured and artificially reconstructed in paintings?**
  Chapter 4 describes various research techniques which are needed for this project, for example artificial aging and BRDF.
- **How can the degradation pattern be digitally reconstructed?**
  In chapter 5 the digital reconstructions which were made of paintings in the past are described. Furthermore, it is explained how BRDF models work and which model is most suitable.

Finally, the results are presented in chapter 6 and discussed in chapter 7. This report ends with a conclusion in chapter 8.

2

Theoretical Background

This chapter focuses on the first sub question of this report, namely *What is the build up of a 17th century painting and what materials are used?* Section 2.1 describes the build up of 17th century paintings, section 2.2 describes the paints used in *Girl with a Pearl Earring* and section 2.3 describes the relevant optics. Finally, section 2.4 describes how colours are quantified.

2.1. Build-up of a painting

The type of painting which is described in this report is painted on a canvas support [6]. To give it stability, the canvas is stretched over a wooden stretcher. Firstly, a size is applied, which is diluted glue that prevents weakening of the painting due to absorption of the binder material from the layers of paint. The canvas is then treated with a ground layer which prevents the absorption of binder into the support even more. Then the layers of paint are applied and the painting may be coated with a layer of varnish [13]. These components can be seen in figure 2.1. The paint layers are discussed in section 2.2 and the other components are discussed in the subsections below.

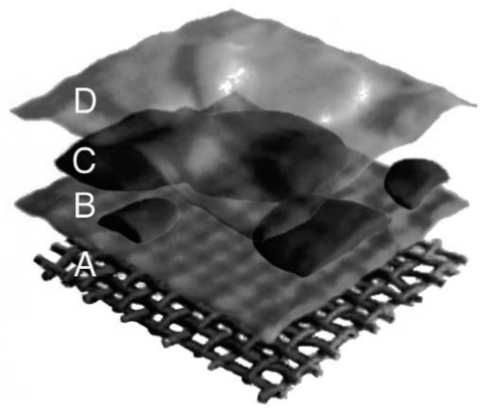


Figure 2.1: The layers of a typical canvas painting, where A is the canvas, B the ground, C are multiple layers of paint and D the varnish. Image obtained from [13].

2.1.1. The Canvas

There is a lot of variation in the canvases used by painters, which can be compared by counting the number of threads per centimeter [14]. *Girl with a Pearl Earring* has a horizontal thread count of 14.8±2.7 threads/cm and 14.6±3.0 threads/cm which is comparable to other works from Vermeer [6] and to other Dutch artists in the seventeenth century [14]. The fibres have not been analysed, but other works from Vermeer had flax fibres in a closed, plain weave. The canvas original size, 44.5 x 39 cm, could have been a standard format since it consists of multiples of the Rhineland inch [6]. The canvas can clearly be seen in figure 2.2, however, it is not the canvas itself which is visible since it absorbs x-rays as an organic material [14]. The imprint of the original canvas in the ground is what can be seen in the figure. When an unprepared canvas is stretched, the fabric will be distorted due tot the differences in stress distribution. This phenomenon, called cusping, is an indication that the unprepared canvas was stretched before it was prepared. Absence of these distortions could show the reduction in size of the painting or that the prepared canvas was cut into pieces for multiple paintings. A primed canvas that was re-stretched for painting after a short period can show secondary cusping, which is smaller in size than primary cusping. During the seventeenth century, a canvas was often laced by a long cord to a strainer [14]. *The Girl* shows evidence of primary and secondary cusping. Possibly, Vermeer bought a prepared canvas, which was stretched and primed with a ground layer. Those canvases were available in the Netherlands in the mid-seventeenth century [6].

Figure 2.2: An x-ray photograph of *Girl with a Pearl Earring* showing the canvas support. Image obtained from [6].

2.1.2. The Ground

In general, the ground was not applied by the painter, but by others [14]. The ground layer prevents the binder absorption into the canvas. In *Girl with a Pearl Earring*, the canvas was on a large framework when the ground was applied. Vermeer only started painting after the canvas was moved to a smaller strainer. From 18 cross-sections, the thickness of the ground layer was found to be approximately 100 μm, and consists of chalk, lead white, together with a fine carbon black. Furthermore, red and yellow iron oxide pigments might be there. The ground is compact and made according to the Dutch stack process, which is concluded by the discovery of large lead white particles with small lead white in between [6].

2.2. Types of paint

The basic ingredients of paint are pigment, to provide colour, and binder, which holds the pigment together. It is possible to add other ingredients to paints, for example to improve optical or textural characteristics or change the working principles [13]. Nowadays, more than 100 different colours of paint are available, but in the seventeenth century this was about fifteen. Pigments were made from raw materials and came from all over the world [12]. Another change over time are the manufacturing techniques. A tube of paint is easily bought in the store, but this was not always the case. The painter, or its assistants, had to mix the pigments with the binder themselves. This gave them the opportunity to explore the possibilities of the paint thoroughly [13].

The colours in *Girl with a Pearl Earring* are [12]:

- Reds (vermilion and red lake)
- Yellows and browns (earth pigments, lead-tin yellow, yellow lake)
- Blues (natural ultramarine and indigo)
- Blacks (charcoal and bone black)
- Whites (lead white)

These will be explained further in the subsections below. The binder which was used for all paints is linseed oil, which was common in the seventeenth century [12]. It is made by pressing the seeds of the flax plant [13]. Some rapeseed oil was found in the painting as well, but that might be contamination. Overall, the paints used by Vermeer are typical for a Dutch painter in the seventeenth century, although he used more ultramarine than most painters did [12].

2.2.1. Red paints

In *Girl with a Pearl Earring* two types of red paint are used, namely vermilion and red lake. The first, vermilion, is used in the skin of the girl [12]. This pigment has been used since antiquity and can be found in nature [15]. However, it is also possible to produce it synthetically, which has been done for this painting and was done on a large scale in the Netherlands at that time [12]. Vermilion is a chemical compound of mercury and sulfur. After heating this compound, the red pigment is visible in the cooled damp. The coverage of the paint is good, but it is a poisonous pigment due to the mercury [15]. The other red pigment used is New World cochineal, which is a red lake. It was imported from Mexico or America and was extracted from insects, who lived and feed on cacti [12, 15]. About 70 000 female insects were needed for 500 grams of pigment [15]. In the painting, cochineal was found in the clothes, flesh tones and lips of the *Girl*, which came from Central or South America [12]. Red lakes are known to fade over time and this could have changed the appearance of the painting [15, 16].

2.2.2. Yellow and brown paints

The most abundant yellow and brown pigments in the painting are yellow ochre and brown umber. The yellow jacket of the girl is mainly painted using earth tones [12]. These pigments have been used since antiquity, for example at cave art, since they can be easily mined from the earth crust. Earth pigments can be found as ores or as deposition products in clay and sand [15]. Yellow lakes are organic like red lakes, but they are extracted from plants [17]. They come from the weld plant, which grew in the Netherlands. It is a pigment which degrades relatively fast, and therefore it is not present anymore in *Girl with a Pearl Earring* [12]. However, the use of the pigment is suggested by the presence of remaining calcium [12, 17]. The pigment might have been used in the blue parts of the headscarf, background and possibly in the yellow part of the headscarf [12] and would then be used to show subtle yellows and greens [11, 16]. The yellow parts of the headscarf contain lead-tin yellow as well, which was probably available to Vermeer due to the ceramics industry in Delft [12]. This pigment made by the heating of lead and tin and is poisonous as well [15].

2.2.3. Blue paints

The abundant use of natural ultramarine is typical for Vermeer [12]. This pigment originated from the stone *lapis lazuli*, which was mined in Afghanistan [12, 15]. Not only this distance made the ultramarine expensive, but also the production was one of the most complex of all pigments [15]. Different grades and prices of ultramarine were available at the seventeenth century and the quality of the pigment used in the painting is suggested to be high. The material is mainly used in the blue parts of the headscarf, but it is also used in the yellow jacket of the girl. The other blue pigment used is indigo, which can be found in the background of the painting. Indigo is a natural pigment, which originates from plants and could originate from Asia or the West Indies [12]. It is nowadays mainly used as a colorant for textile and is still used for the coloring of jeans [15].

2.2.4. Black paints

Black pigments are produced by charring bones or plants [12] and it has been known since antiquity. Animal bones or antlers produce bone black and charcoal is produced by coal of oil [15]. Charcoal is mainly used in the background of *Girl with a Pearl Earring* and bone black is mainly used in the face of the girl. Both have been used in the dark underlayers of various parts of the painting, however, they could not always be distinguished [12].

2.2.5. White paints

The only white pigment used in the painting is lead white [12]. It has been used since the ancient Egyptian civilizations and has been used until the twentieth century. However, this pigment is poisonous and therefore it cannot be used anymore nowadays [15]. Vermeer used lead white on the pearl earring, eyes and the Girl's collar. It was also mixed with other pigments and has been used in most parts of the painting. The lead white in the painting originates from England [12]. Two particle sizes were used by Vermeer, namely Hydrocerussite and the finer cerussite [10].

2.2.6. The Varnish

A varnish is a coating applied when the painting is finished. Firstly, it is transparent and protects the paint layer from pollutants, abrasions and dirt, and secondly it may change the reflective properties of the painting. Not all paints may have dried in a similar way and a varnish can make this uniform [13]. Since *the Girl* has undergone several cleaning and restoration treatments, no remains of the original varnish layer remain, if Vermeer applied any. During a restoration process that involves cleaning, the old varnish is removed and new varnish is applied. Currently, several layers of dammar varnish are present, which were applied in 1994 during the restoration [3].

2.3. Optics of paint layers

The interactions between light and the paint layers lead to our perception of a painting. It shows us the texture, thickness of the paint and the transparency of the paint layers. The interaction of light with the ingredients of the paint show us the colours of a painting. The effects of the reflection, refraction and absorption of light with a painting are explained below.

Incident rays which are reflected can show two different surface properties. Reflected light rays from a smooth surface produce a smooth, clear image because they are parallel to each other. Reflected rays from a rough surface behave in another way, all rays are reflected in a different direction, making the image dull.

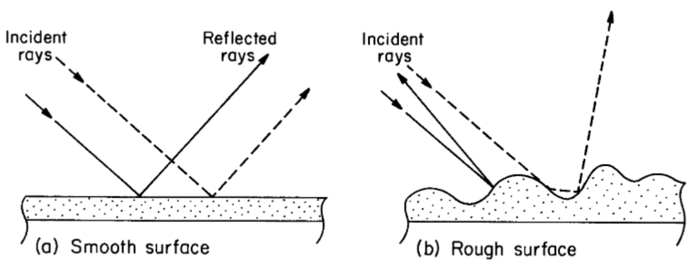


Figure 2.3: The difference between reflection from a smooth (a) and a rough (b) surface. Image obtained from [13].

When light hits a surface or interface, it will reflect only partially. The other part will be transmitted through the next layer of paint until the next interface is reached. This happens at every layer of the paint and is called refraction.

Refraction of light rays happens when an interface is crossed where a change in light velocity takes place. For example, the velocity of light decreases by 66% when the light enters binders such as linseed oil, giving a refractive index of 1.48. Overall, paints have refractive indices from 1.33 in water-based materials to 2.5 for titanium white. The difference between the refractive indices of the pigment and the medium can result in scattering of light, which influences the transparency of a paint layer. If this difference is large, then the deflection of light is higher and the other way around. The amount of scattering depends further on the size of the pigment particles. Scattering goes easier in paints which have pigments of the same size as the wavelengths of visible light. An increase in density of the particles also increases the scattering [13].

Absorption of light is the reason objects have different colours. Specific wavelengths of light are absorbed by a material, and then the photons which are not absorbed will be reflected or scattered, resulting in a colour specific to the material. The density of the pigment particles determines the amount of light that is absorbed. The higher the density, the more absorption and the less transmitted light. The latter will decrease with depth as well.

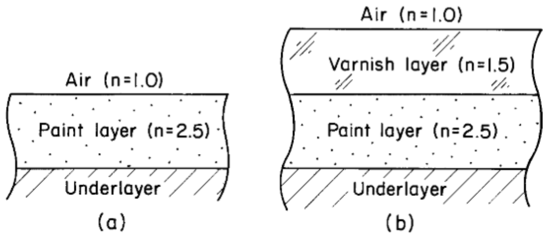


Figure 2.4: A cross-section of a paint without (a) and with (b) a varnish layer applied. The refraction indices are shown as well. Image obtained from [13].

Adding a varnish layer to a painting prevents scattering, since the surface is flattened. However, since the differences between the refractive indices of the layers are smaller, as can be seen in figure 2.4, more light will be transmitted into the paint layer and absorbed by the pigment. This will cause a deeper and richer colour. Painters can use a glaze if they want this effect in their painting [13]. *Girl with a Pearl Earring* has such a glaze as well. It was applied on the background and contains indigo, yellow weld and copper. Figure 2.5 shows the layers of the painting, the glaze layer can be seen here as well [3]. This layer has deteriorated, and will be discussed in more detail in subsection 3.2 and 3.7.

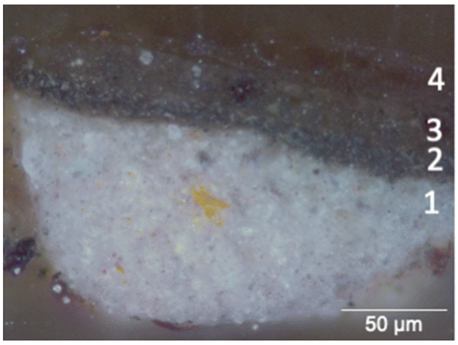


Figure 2.5: A cross-section of a sample from the background of *Girl with a Pearl Earring* seen by a light microscope, bright field. The layer which can be seen are (1) the ground, (2) underlayer, (3) glaze and (4) the varnish from a restoration. Image obtained from [3].

2.4. Fundamentals of colour quantification

The perception of colour is done by a combination of the human eyes and the neural system in the brain. Photoreceptors in the retinal membrane in the back of the eye receive the input. Two different types of receptors exists: rods and cones. Rods are extremely light sensitive and do not detect colour. Cones handle the colour vision. There are three different types of cones, namely short, medium and long sensitive cones. Commonly they are abbreviated to S, M and L cones. Afterwards, the brain will interprets the signals. These signals are commonly known as light, but are actually electromagnetic rays in the visible region of the spectrum. The electromagnetic spectrum can be seen in figure 2.6.

Normally wavelengths between $\lambda = 360\ nm$ and $\lambda = 830\ nm$ are visible by the human eye. The attribution of a colour to an object is only possible with an observer, it is a sensation experienced by a viewer which is coupled to a stimulus causing the sensation. This is called the *stimulus error*.

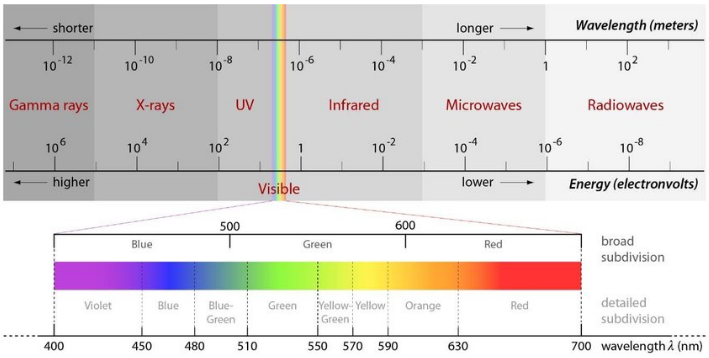


Figure 2.6: The full electromagnetic spectrum. Image obtained from [18].

The Commision Internationale de l'Eclairage (CIE) is responsible for the standardization of colour terminology and metrics. In colour imaging and the printing industry the colour space which is mostly used is CIELAB. Figure 2.7 shows the build-up of this space. It consists of three axes, namely L^*, a^* and b^*. L^* represents the lightness, ranging from 0 for pure black to 100 for pure white. a^* stands for the red-green axis, where a positive value stands for redness and a negative value for greenness. In a similar way, b^* is the yellow-blue axis, where a positive value stands for yellowness and a negative value stands for blueness. The colour difference ΔE between two different samples is:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2.1}$$

where ΔL^*, Δa^* and Δb^* are the distances between the two different samples on the axes shown in figure 2.7. A ΔE of around 2.3 is a *just noticeably difference* (JND). A limitation of this system is the hue correlation in the blue areas [19].

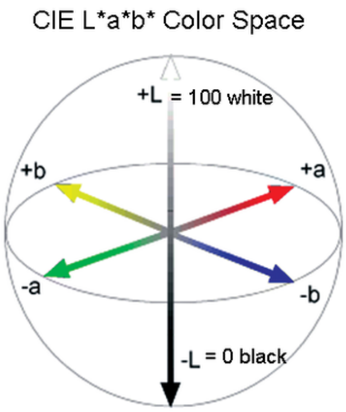


Figure 2.7: A visualization of the CIELAB colour space with the L^* (black-white), a^*(red-green) and b^*(yellow-blue) axes. Image obtained from [20].

However, an object which has a specific colour is not isolated. Many variables affect the colour which is observed. These are the interactions of a colour. Examples of parameters which influence these spatial relationships are the saturation, value and temperature of the adjoining colour. For example, warm, saturated and light colours advance towards the viewer, while cooler, neutralized and darker colours recede to the background. Furthermore, the concept of afterimages is important. When two colours are complementary, a luminous transparency appears as the complementary colour. It is like a colour filter. A result is that complementary colours are more intense together since they amplify each other. This changes the perception of the chosen colours and so of paintings [13].

3

Previous Research on *Girl with a Pearl Earring*

This chapter focuses on the sub question *What types of degradation mechanisms can occur in paintings and which are relevant for this painting?* It describes the various types of degradation mechanisms which can occur in paintings.

Paintings can age in various ways. The first five sections will describe multiple mechanisms which can occur, such as fading of lakes and lead soap formation. Finally, section 3.6 will describe how these colour changes can be prevented and section 3.7 describes how the perception of a painting can change.

3.1. Fading of Lakes

Between the fourteenth and nineteenth century, lake pigments were used regularly in western European paintings and were seen as crucial in the choices of the artist's paint because it expanded the artists palette [16]. Yellow lakes were used to show subtle yellows and greens, and red lakes were used for transparency and depth [16]. However, it was already known in the seventeenth century that the pigment was unstable [17]. Over time, the colour will be lost due to the exposure to light, which changes the appearance of the painting [16]. If a cross-section is made, a colour difference can be seen between the top and the bottom part of the sample [3, 16] as can be seen in figure 3.1.

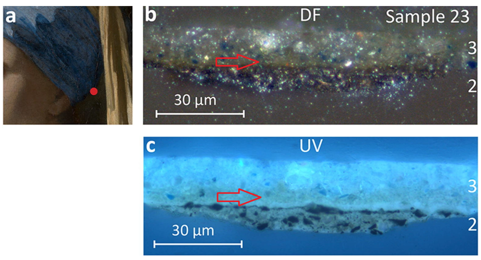


Figure 3.1: A cross section from the painting. a) Location of the cross section in the painting. b) The cross-section seen with a light microscope, dark field. c) The cross-section seen in UV light. The bottom part of layer 3, indicated by arrows, are more yellow than the top part. Image obtained from [11].

It is possible to simulate this behaviour by exposing samples with lakes to artificial daylight [16]. This process will be described in more detail in section 4.4. Afterwards, it can be measured how much the colour has changed, of which an example with various yellow lake can be seen in figure 3.2a. It can be seen that the colour change approaches a constant value after a number of hours which is dependent on to the substrate and the type of lake. Figure 3.2b shows the change in the redness (a*) and yellowness (b*) for some of the samples in figure 3.2a. It can be seen that especially the yellowness changes significantly after artificial aging, which is expected since only yellow lake pigments were tested.

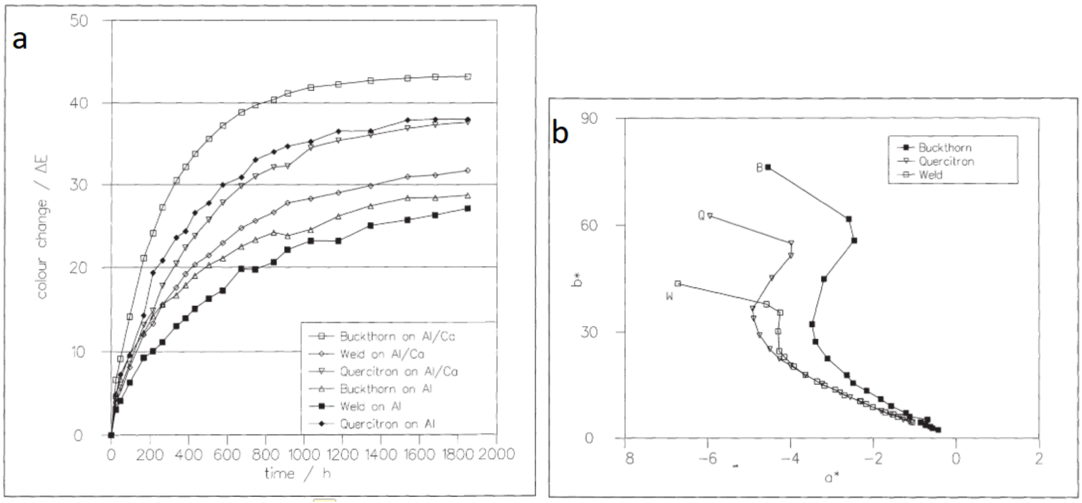


Figure 3.2: a) The colour change of samples plotted versus the time they had been artificially aged for yellow lake pigments on aluminium/calcium or aluminium substrates. b) The change in redness (a*) and yellowness (b*) for pigments the pigments in a) which were on aluminium/calcium-containing substrates. Images obtained from [16].

The disadvantage of taking cross-sections is that it damages the painting. Furthermore, it is not certain that these samples are representative for larger areas. Therefore non-invasive techniques research techniques are preferred [9]. An example is the use of X-ray Fluorescence (XRF), which is explained in more detail in section 4.1. Chalk could have be present as a substrate of a yellow lake, which has since faded.

For *Girl with a Pearl Earring* the XRF map, as can be seen in figure 3.3, shows the calcium presence in the painting, which then suggests the present of a faded yellow lake [11]. However, not all calcium indicates a yellow lake, it can also be there from a carbon-based bone black pigment. Cross-sections show that yellow lakes have been used in the background and the blue headscarf of *the Girl* [12].

Figure 3.3: The XRF map of calcium for *Girl with a Pearl Earring*. The red arrow shows an example of the location where the calcium indicates a faded yellow lake. Image obtained from [11].

The use of red lake has been detected by molecular fluorescence imaging spectroscopy (FIS), which will be explained in more detail in appendix B. Additional measurements were made using FORSc(fibre optic reflectance spectroscopy) which is also explained in appendix B. The measurements showed that the red lake was insect-based with an aluminium substrate, which can be cochineal or lac for example. It has been used in the lips and the skin of *the Girl* [7].

3.2. Fading of indigo

In 17th century Netherlandish oil paintings it is common to see fading and discolouration of indigo paint. The chemical breakdown of the *indigotin* component is what causes this process. Many external factors like light intensity, wavelength distribution and air pollution have been identified. Since internal factors like the preparation method, the type of binding medium, layer thickness, pigment volume concentration and mixture are important for yellow and red organic pigments, as described in section 3.1, it is expected that it is also important for indigo. However, it is not clear to what extent this is true. This may be due to the fact that fading of indigo is not a problem when used as a textile dye.

Experiments on the fading of indigo showed that the purity of the pigment used is mainly what determines the lightfastness. The discoloration can be seen sooner when the colour saturation is lower. Therefore, paints made from natural indigo fade faster than those made with synthetic indigo. Up to the end of the 17th century, painters were advised to use indigo only for the underlayers. Following the example set by Frans Hals, Vermeer started to use indigo in his works, like other painters in his time. There are various techniques to use indigo in the top layer of a painting. It can be mixed with lead white or chalk, smalt or with yellow lake. The latter was done in *Girl with a Pearl Earring* and formed a green glaze in the background of the painting. The colour was characterised as *a sad green* by a 17th century treatise [21]. However, both pigments faded and nowadays the underlayer is the primary colour to be seen.

The glaze was originally relatively flat, but nowadays the effects of ageing can be seen, namely cracking, cupped paint and delamination. A small band of glaze in the right top corner is thicker, as can be seen in figure 3.4, which is probably due because of a thinner underlayer. In this band, the lead concentration is lower. Vermeer did vary the amount of lead, which he used to create highlights and shadows in the background. This line indicates a curtain, which was painted in the background. Due to the degradation of indigo and yellow lake, it is nowadays almost invisible to the naked eye [3].

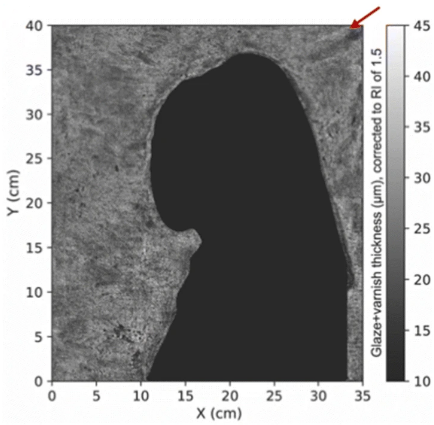


Figure 3.4: A MS-OCT glaze + varnish layer thickness map for the background of the painting. The arrow indicates a curtain, which used to be visible in the painting, but cannot be seen anymore with the naked eye. Image obtained from [3].

3.3. Lead soap formation

As as result of a chemical reaction between lead ions in pigments and saturated fatty acids from the drying oil of the binder, a phenomenon called lead soap formation can occur. The diffusion of those fatty acids is the driving force which controls a nucleation process. In the first step, the reaction is probably reversible and forms an amorphous nucleus, but later a crystalline structure is formed by an irreversible reaction. Then the structure is large enough to penetrate the paint surface and deform the layers of paint. Due to this nucleation process, strains will be introduced in the paint, which can cause flaking of the paint layers [22]. Another consequences is that the refractive index of the oil increases, thus making it closer to the pigments' refractive index. This causes the paint to become more transparent [21] and therefore appears more dark, as the light can penetrate deeper into the paint [10]. This causes the underlying paint layers to become more visible, which can change the appearance of the painting in a large way. However, it is difficult to decide if parts of the underlying paint layers might have been shown on purpose. Overall, the process is assumed to gradually take place over several decades. Therefore it is suggested that painters in the 17th century did not know about the increasing transparency or understood the effect of the increased transparency [21].

In *Girl with a Pearl Earring* the carboxylic acid groups have reacted with the lead white pigments. This can be seen in the dark shadow parts since the darker underlayers have became more visible. The effect is less noticeable in the light pink flesh tones since these paint layers are thicker and the underlayers have a lighter colour. The darker parts would have increased the contrast between the lit and shadow parts of the face [10].

3.4. Yellowing of oil binder

The oil binding medium has as tendency to turn yellow over time. In the dark, a process which forms chromophores as degradation products takes place. This happens as the oil dries and ages and makes it appear yellow. Furthermore, exposure to light might result in bleaching of discoloured paint layers. The extent of discolouration depends on the type of oil, linseed oil will discolour more than walnut and poppy oil. Discolouration also depends on the preparation technique. Since the amount of discolouration depends on the proportion of oil in the paint, pigments which absorb much oil are more susceptible to the degradation process. However, the result of the yellowing also depends on the colour of the pigments, on 'warm' yellow and red paints the discolouration is barely visible, whereas blue and white paints show a great difference as they will look more greenish. Painters knew about the yellowing of oil in the 17th century and were advised to wash the oil before use. Additives like sawdust, snow, powdered chalk, breadcrumbs or alums were added to the water to absorb mucilaginous material [21]. It is not clear if *Girl with a Pearl Earring* suffered from the yellowing of the linseed binder. It might have occurred in the background before the 1994 restoration, but due to the adjustments made then it is not visible anymore nowadays [4].

3.5. Other pigments

There are several other pigments which discolour over time. A first example is smalt, that is made from potassium enriched glass, to which cobaltarsenate is added at a temperature of 1200 °C. This pigment fades in a slow pace and was used as alternative for more expensive ultramarine and azurite, but it has a low hiding power. The discolouration may have three different reasons. Firstly, the paint layer will oxidize, resulting in a converging refractive index for the pigment and the binder. This decreased the scattering of the light. Secondly, the potassium in the pigment could have leached into the binder. This could have happened to the cobalt ions as well as a final factor. However, this final explanation is disputed [23]. No smalt was used in *Girl with a Pearl Earring* [12].

Another pigment which can discolour is verdigris, which are a range of corrosion products of copper varying between greeen and blue-green. It is mainly used in green glazes, when the verdigris reacts with a varnish. In the 15th-17th century, painters used this colour mainly to depict draperies. However, nowadays the colours often have turned brown. Verdigris can react with other pigments, especially in aqueous media. In oils it is less likely, however, pigments might reacted with others in different layers. In the 17th century, the use of verdigris decreased [21].

For *Girl with a Pearl Earring*, Kühn concluded in 1968 that verdigris was present in the green glaze layer in the background of the painting, since copper was measured there. However, research in the 1990's found no verdigris when two samples were analysed. *The Girl in the Spotlight* showed that there is only a small quantity of copper in the painting and that there were no copper-rich particles in the sample of the background. It is not clear where the copper originated from, but it is possible that they accelerate the drying of the painting. They would have little effect on the colour and translucency. Two suggestions of the origin of copper were made, namely that a small quantity of verdigris was present, but dissolved in the oil of the medium. Another option would be the use of a copper pot to heat the binding medium [3].

Finally, almost all pigments used in *Girl with a Pearl Earring* are used in mixtures. Therefore the colour change per location in the painting can vary, since the other colours may respond different to the effects of time.

3.6. Prevention of colour changes

Painters in the 17th century knew that the colourfastness of pigments varied. Therefore they tried to recognise durable pigments, since the differences in durability could be major. However, this was not a fully adequate method. Furthermore, some pigments faded slowly, so painters did not have a chance yet to see the discolouration since the pigments were not used for such a long time. They did know that sunlight increased the fading speed of some pigments. They also knew that cleaning with water was damaging to certain pigments. The choice between the discolouring and permanent pigments was influenced by its handing properties, the price and the available alternatives. In some instances there was no choice than to use a pigment which would fade. Sometimes those pigments were only used in the underlayers, where they would be covered by other pigments. If they were used in the top layer, specific techniques were applied. For example, indigo was mixed with some lead white or the varnish was applied locally, which probably was a suitable method [21].

3.7. Historical context

Perception of artworks refers to *the relationship between the artwork's materiality as the starting point of one's personal emotional connection with the object and the various meanings the viewer might attach to it* (literally obtained from [24]).

Due to the changing appearance of a painting because of the discolouration of pigments, the perception might change. This can be seen in multiple aspects of a painting. Firstly, the suggestion of space can change. Contrast or brushstrokes can show depth in a painting, while they might not be visible anymore in the discoloured painting. Increased transparency in a paint layer has also consequences for the imitation of textures in the depicted scene. It can cause a paint layer to become flat and incomprehensible. The loss of depth is the most evident consequence of paint discolouration in paintings. The reason depth can be lost due to discolouration is because colours interact with each other. Normally, warm and saturated colours advance to the viewer, while cooler and darker colours tend to recede in the background. Saturation is defined as the purity of a hue, and reducing it leads to a more neutralized colour [13].

A consequence which is more difficult to see is the possible loss of colour harmony in a painting. Colours have been chosen in a balanced way, which produces an ensemble in a painting. This could be lost if some of the colours change. Currently, spatial illusion and colour harmony are seen as separate concepts in a painting. In the 17th century, however, they were connected and are referred to as *Houding*. It consists of subtle nuances in dark and light tints, strong and weak colour nuances and the difference between the objects which are clearly defined in a painting and those who are not. This makes it difficult to use strong colours, since they have to be balanced [23]. Furthermore, objects were supposed to have sharp edges, creating a contrast between them. If not, the painting could become 'an obscure mass' where things would 'appear entangled'. This last concept means that objects and colours in a painting do not stand on its own, there are relations between them. If they would not be there, the painting would become a uniform image. The goal is for viewers to look through a painting, instead of seeing everything in just one look. Willem Goeree wrote about *Houding* in his book *Inleyding tot d'Algemeene Teykenkonst* in 1668 *Houding is one of the most essential things to be observed in a Drawing or Painting; since it gives the same sensation to the eye, that we enjoy in the contemplation of natural objects. For whenever Houding is not found in representational images, such Drawings and Paintings are senseless, and more than half dead*. (Literally obtained from [25]). This shows the importance of the concept in the 17th century, calling objects 'senseless' and 'more than half dead' if they don't achieve *Houding*. Goeree's suggestion to avoid this is to create a natural flow inside the painting, extending to the viewer. Another possibility is to create light effects. It can create a three dimensional effect by the colour contrast of the chosen paint colours. An example of that can be seen in figure 3.5, a painting by Philips Koninck. The contrast between the bright sunlight and the dark clouds in the sky creates depth. Another example is the yellow part of the headscarf of the *Girl*. The fabric looks more realistic and identifiable due to the added dark shadow parts. The concept of *Houding* was mainly important in the Dutch arts, other countries did not find it as important [25]. In the 18th century, the concept of *Houding* was abandoned [23].

To this day, there is a discussion if Vermeer used a camera obscura. Firstly it was hinted by Wilenski

Figure 3.5: The painting *A Panoramic Landscape* by Philips Koninck. The bands of sunlights against the clouds in the sky creates a sense of depth, thus leading to *Houding*. Picture obtained from the The J. Paul Getty Museum, Los Angeles.

in the 1920's, because of the foreground objects which would be distorted enlarged. Mayor was more certain in 1946 citing, naming the blended colours and the highlights on the foreground objects. The technical knowledge could be provided by Antoni van Leeuwenhoek, who lived in Delft at the same time as Vermeer [26]. Another option is that Vermeer got the knowledge from the Jesuits, who where his neighbours at the Oude Langendijk in Delft. Due to his catholic wife, contacts between them and Vermeer seem plausible. Within the Society of Jesus, it is known that they have knowledge about optics. Furthermore, there are many clues that father Isaac van der Meye, who also lived and died in Delft, used a camera obscura for his drawing *Portret van een oudere vrouw*. Characteristics of a camera obscura begin to appear in Vermeer work within a year of Van der Meye's death [27]. Did his instrument move to Vermeer's studio?
Seymour conducted an experiment in 1964 on *The girl in a red hat*, also painted by Vermeer, and noticed that the highlights in the painting resembled the ones on a photo [26]. According to Wheelock, the accentuated perspective and the heightened contrasts of dark and light were attractive to Vermeer as well. Wadum did not believe in a camera obscura due to the vanishing points in many of Vermeers paintings, since they were actual holes with pins stuck in the paint [28]. Of course, Vermeer did not have to use a camera obscura directly, he also could have wanted to mimic its effect. The *Girl in the Spotlight* project gave new insights in this discussion. For example, on the function of the addition of the glaze layer on the background. It served a double purpose by firstly scattering reflections and therefore enhancing the darkness of the background. Secondly, the glaze layer flattens the surface and the brushstrokes from the paint layers beneath are covered. This creates a sharp contrast between the background and the figure, not only in colour, but also in the thickness of the paint layer. Especially the collar of the *Girl* is painted with some *impasto*. This creates a photographic effect, namely a low dynamic range. This could have been inspired by a camera obscura [3]. Another example is the use of different types of lead white. Hydrocerussite with a larger particle size is used more in the underlayers and on the lit parts of the face, while the finer cerussite is used more on the top layers and in the shadow parts of the face. Since cerussite is less opaque than hydrocerussite, and it is applied more thinly, the underlayers still play a role in the painting [10]. This causes a contrast between the lit and shadow parts of her face.

Combining both the concept of *Houding* and the use camera obscura work well together. A characteristic like the creation of highlights is suitable for both. A low dynamic range from a camera obscura reduces the greyscales and thus increases the contrast. This is important for *Houding*. The appearance of a living person creates a natural flow, as if the person is standing in front of the viewer, or in front of a camera? Of course, it can never be determined for sure if Vermeer actually used a camera obscura, however, it can be said that the options it creates would fit in the spirit of the age.

The *Girl* has also suffered from changes in the paint and has a different appearance then it did in the 17th century. As mentioned in the previous sections, colours have faded and changed, and therefore the painting does not look like it was intended anymore [12]. The colour harmony and spatial illusion changed, which would have been more disturbing to a 17th century viewer then it does to us [21]. However, the changes can still be seen and have an effect on the current day viewer. Due to the fading of the lakes, the paints have a lower saturation. As mentioned before, this neutralized the colour leading to a lower contrast. Strong colours disappeared, losing balance in the painting. The background is not as smooth and dark as it used to be anymore. The large contrast with the face and the white collar disappeared. The collar is now in need of a counterpart. The contrast is what leads to the three dimensional effect, meaning that this decreased over time. Overall, time has had a negative effect on the *Houding*. This means that the perception of the painting changed significantly, because the *Girl* would have popped out of the painting more. Nowadays, the painting is more of a flat image. This also means that it is more difficult to determine if a camera obscura was applied or not. Did the *Girl* look more like a photo in the 17th century? The arguments are complementary as for the *Houding*.

There is another aspect of perception that needs to be taken into account. An ultimate goal of the *Girl in the Spotlight* research was to develop 3D prints that approximate *Girl with a Pearl Earring* when Vermeer just finished painting it [12]. This is called a reproduction and is defined as a replica which does not need to have historically accurate materials and technique. This opposed to a reconstruction, which should resemble the working process of the painter as closely as possible. Reproductions might also change the perception of an original painting. In the current Western culture, they are seen as anti-authentic because of them the artwork is no longer unique. However, due to the fast development of technology the perception of reproductions changes. Reproductions and reconstructions can be used to understand the original object and therefore be authentic. Perception research about *Girl with a Pearl Earring* showed that reproductions can seen as a positive addition in museum environments. They should add something to the presentation of the original artwork and should be easily understandable. Physical reconstructions were preferred over digital reproductions in these circumstances. However, material similarities are important for research [24]. This is important for the presentation of the results of this project. A digital model presenting the colour change can be made to show various possibilities.

Overall, it can be said that the look of *Girl with a Pearl Earring* has changed significantly over time. Various pigments like red and yellow lakes and indigo have faded away. This has had a serious effect on the perception of the painting nowadays. For example, the contrast used to be much larger in the painting, leading to *Houding* in the painting. This would have been more disturbing for a 17th century viewer than for someone today, however, it can still be seen. It is also liked to the discussion if Vermeer used a camera obscura or not. Both concepts use the similar arguments, like the use of highlights and the more living, 3D effect which is nowadays not visible anymore. Altogether, it would be very interesting to see how the colour changes apply to *Girl with a Pearl Earring*, to see if more *Houding* is in the painting and to visualize the probable changes on the painting.

4

Methods and Techniques

This chapter describes the sub question *How can colour degradation be measured and artificially reconstructed in paintings?* Firstly, x-ray fluorescence (XRF) will be discussed in section 4.1 and reflectance imaging spectroscopy (RIS) in section 4.2. These measurements were not done for this project itself, but they were executed for the *Girl in the Spotlight* project and the results have been used. Secondly, the preparation of the samples will be explained in section 4.3. Then the process of artificial aging is explained in section 4.4, the colour measurements in section 4.5 and finally the BRDF is explained in section 4.6.

4.1. XRF

X-rays have wavelengths of around 1 nanometer, this makes the energy of the photon to be a thousand times greater than for photons in the visible spectrum [13]. Techniques using x-rays are x-ray fluorescence (XRF), which is discussed in this section, and x-ray powder diffraction (XRPD), which will be explained in appendix B.

Because of the high energies of x-rays, they pass through the paint layers relatively easy [13]. However, some photons are absorbed, which provides an option for pigment identification [13]. This process can be seen in figure 4.1. It shows the absorption and following emission of x-rays in a schematic view. A common transition is when an electron is ejected from the K shell and then the vacancy will be filled from the L level. The emitted x-ray is then known as a $K\alpha$ line. Another option is the emission of the $K\beta$ line when the K shell is filled by the M level instead of the L level [29]. These electron levels are unique for each atom [13]. The energy of the x-ray which is emitted, and therefore the difference between the electron levels can be used to calculate the corresponding element using Moseley's Law [29]:

$$\frac{1}{\lambda} = k(Z - \sigma)^2 \tag{4.1}$$

where λ is the wavelength of the x-ray, k a constant for a particular spectral series, Z the atomic number and σ a screening constant [29]. The amount of pigment present is indicated by the number of x-ray lines measured [13].

These properties of atoms have been used in various research techniques. Nowadays, one of the most used in pigment characterisation is x-ray fluorescence (XRF) [30]. Important reasons are the possibility to work *in situ* [30, 31], the non-invasive manner [5, 30] and the possibility to look at the sub-surface layers [5]. It can be used in small regions (micro-XRF) or larger sections (macro-XRF) [30]. Scanning macro XRF (MA-XRF) is mainly used to scan full or large parts of paintings. This is done by a moving measuring head on a *XY*-motorised frame, where it can scan a painting line by line, pixel by pixel [5]. It will provide data which can be used to compute maps which show the distribution of various chemical elements. Examples of software that can be used are PyMca and Datamuncher [7, 30]. These maps can be used to indicate the corresponding pigments. Since all layers are mapped in one output value,

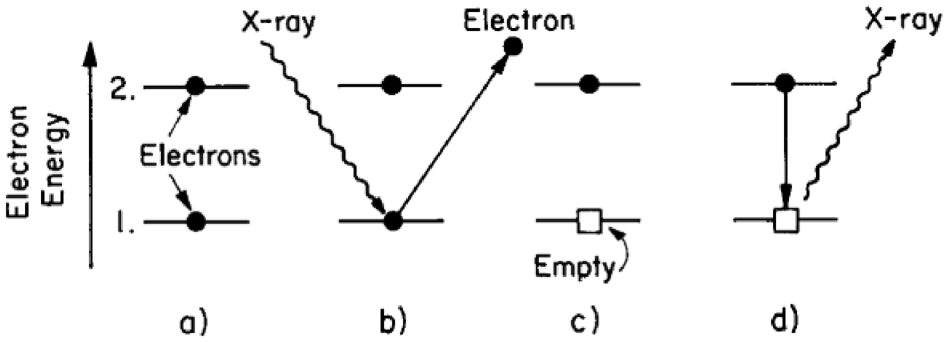


Figure 4.1: The schematic overview of the x-ray emission process: a) two levels are filled with electrons, b) the electron from level 1 is ejected by an incoming x-ray, c) level 1 is in an empty state and d) the electron from level 2 falls back to level 1 and emits an x-ray. Image obtained from [13].

it is not known on which layer the measured element is present. Techniques using molecular data can complement this, for example RIS [5] which is explained in section 4.2. XRF can show modifications and surface restorations and produces high resolution element distribution maps. Another benefit of the technique is the detection of elements of a low atomic number [30], although elements should be heavier than silicon [7].

4.2. RIS

Reflectance imaging spectroscopy (RIS) is a technique which can provide information on a molecular level and therefore it is used in combination with XRF [5, 7]. It is mostly used in two different spectral ranges, visible-to near infrared (VNIR, 400-1000 nm) and shortwave infrared (SWIR or NIR, 967-1680 nm) [5, 7]. Some pigments, like blues, greens and earths can be distinguished using VNIR since they change slowly with wavelength [32]. For pigments which transitions vary sharply, SWIR has to be used, because it has a higher resolution [32].

Infrared waves have wavelengths which are greater than 700 nanometer. Therefore their energies are low and they are not absorbed by most pigments [13]. Due to the increase in wavelength, the reflection of the pigments is low, because of the decrease in the amount of scattering for pigments. Since the photons are not absorbed or reflected, they penetrate through paint layers until they reach the ground layers. The photons are reflected by the white pigments in the grounds, but they are absorbed by the dark underdrawings. These differences between reflection and absorption can be detected and used to gain information about the composition of the layers of the painting [13].

A reflectance spectrum of a paint mixture cannot be modelled as a linear mixture of the components separately. Therefore it is necessary to 'unmix' their spectral components [33]. This is done by the construction a model of light transport through a turbid medium. The Kubelka-Munk (KM) theory is an approximation of the spectral reflectance of paint layers and it relates the effective absorption (K) of the layer and the effective scattering coefficients (S) to the diffuse reflectance (R) [33]. Assumptions for the KM theory are:

- The particle sizes are much smaller than the layer thickness
- The area of the paint layer is much larger than the thickness
- The light propagation and illumination are diffuse

The reflectance can be calculated with:

$$R = \frac{1 - R_g[a - b\coth(bSh)]}{a + b\coth(bSh) - R_g} \tag{4.2}$$

where $a = (K + S)/S$, $b = \sqrt{a^2 - 1}$, h the thickness of the layer and R_g the substrate reflectance [33].

The absorption and scattering coefficients can be related to the reflectance in the limit of a paint layer with infinite optical thickness R_∞ by:

$$\frac{K}{S} = \frac{1 - R_\infty}{2R_\infty} \tag{4.3}$$

The KM theory is then corrected by Saunderson's correction to adjust for the interfaces of the paint and air [33]. The reflectance of the mixture is determined with a linear combination of K/S. Then a non-negative least squared fit is used to find the concentrations of single pigments [33] by comparing them to a database with reference spectra [34]. To do so, false colour images are generated as well [34] which are constructed with three bands [32]. Important parameters which can affect the identification are the particle size, concentration, binding medium and the surface dirt and varnish [33].

The output data of a RIS measurement produces image cubes with spectral channels that can span both the VNIR and SWIR regions [7]. Such a spectral basis set is called an endmember [34]. Taking the first derivative with respect to the wavelength of the image cube can help in the separation of pigments with overlapping spectral features [7]. Figure 4.2 gives an example of how such a procedure is used to separate between pigments. It can be seen that on the left side of the face, the 'red' endmember, more vermilion is present, while on the right side, the 'green' endmember, more ochre is present. The 'blue' endmember on her neck is dominated by ochre [7].

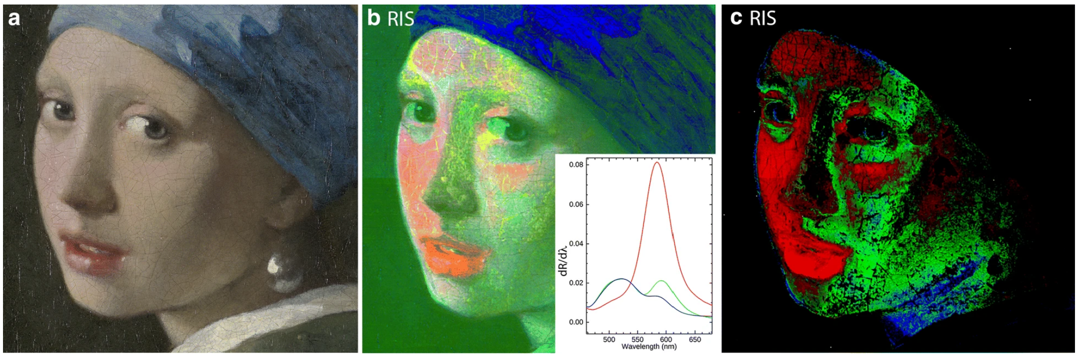


Figure 4.2: An example of the use of a false colour image with RIS. a) The visible light photograph, b) the false-colour first derivative with the endmember spectra used in the insert and c) map of the first derivative spectral endmembers with 'red'= mainly vermilion, 'green'= ochre with vermilion and 'blue'= mainly ochre. Image obtained from [7].

4.3. Sample preparation for artificial aging

The reconstructions used in this research are made by Technical Art History student Mané van Veldhuizen. She did this as part of her masters thesis at the University of Amsterdam. The locations picked for the reconstructions were chosen in cooperation with each other. The samples were made with a reconstruction of the paint used by Vermeer, with an aim to replicate them as well as possible using historically appropriate materials. The pigments that he used were determined during the *Girl in the spotlight* project. The reconstructions can show the properties of the original paint, like the colour, aging behaviour and handling properties. However, all historical recipes have their limitations and it is not possible to make a perfect copy of the paints [35]. In Europe, there are a few locations were historical pigments can be bought like oil mill 'Het Pink' in Zaanse Schans or Kremer Pigmente in Germany. No structural or chemical research was done on the reconstructions. There is already much knowledge about the aging mechanisms of these reconstructions [16, 21], which was already explained in sections 3.1 and 3.2. As this was considered adequate and due to time constraints, the decision has been made to skip this step for this project.

Cross-sections from the painting were used to determine the necessary ingredients for the reconstructions, as well as non-destructive techniques as XRF and RIS. With all these information, the pigments used by Vermeer were determined as well as possible and can be found in [7].

There are three focus points of *Girl with a Pearl Earring* which were studied in more detail, namely the blue headscarf, background and her face (including the lips). All the top paint layers on those locations

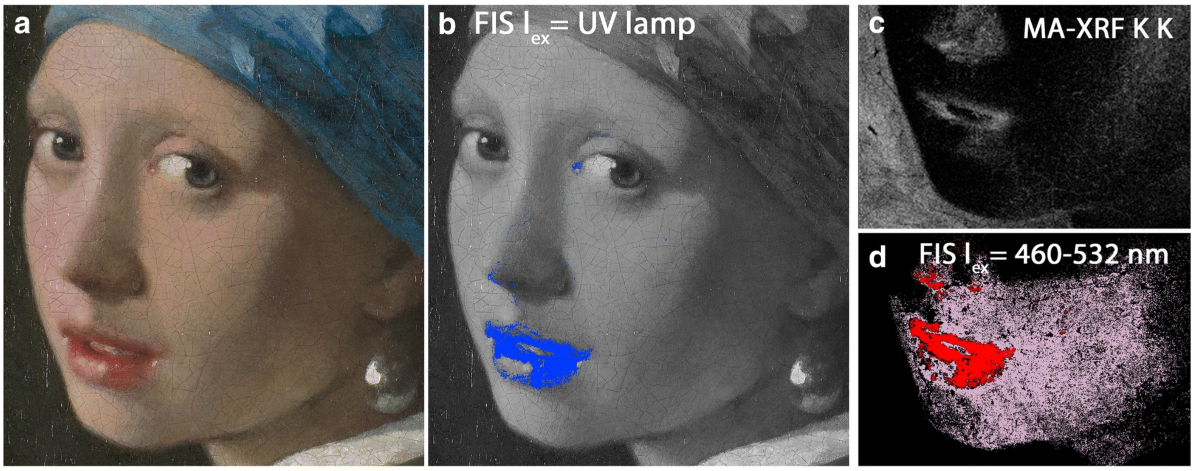


Figure 4.3: a) visible ligth photograph of *Girl with a Pearl Earring*. b) Red lake distribution showed using a fluorescence endmember obtained with UV light. c) XRF map of potassium. d) Two fluorescence endmembers showing red lake distribution. Image obtained from [7].

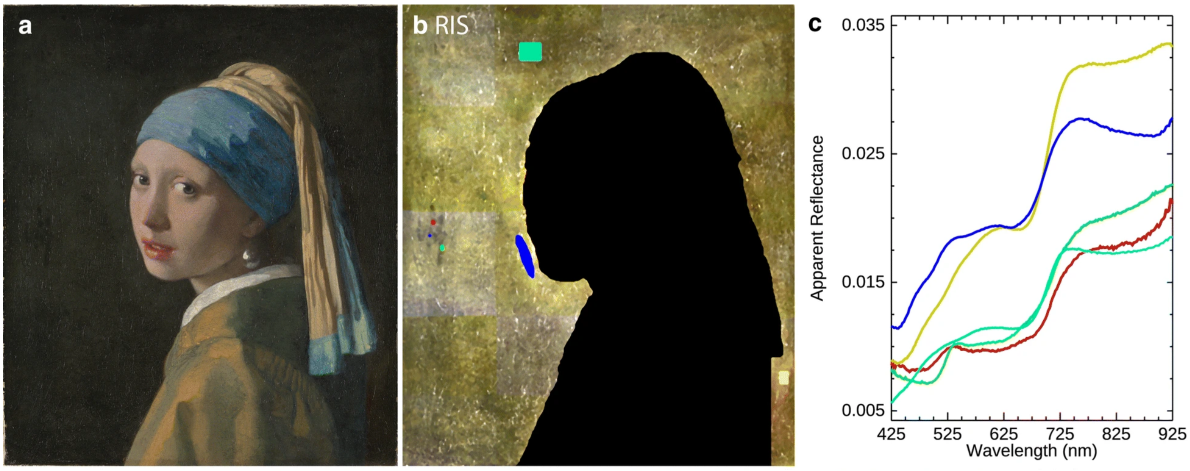


Figure 4.4: a) visible light photograph of *Girl with a Pearl Earring*. b) False colour reflected image with several Regions of Interest (ROIs). The figure was masked. c) Corresponding reflectance spectra to the ROIs of b. Image obtained from [7].

presumably contained lakes when Vermeer painted them, as explained more in more detail in section 3.1. The background and blue part of the headscarf contained yellow lakes, as shown in the XRF map of calcium in figure 3.3. Red lakes are present in the lips and the flesh tones. Indirect evidence for the use of red lakes was found using the XRF map of potassium, as seen in figure 4.3c. Using FIS, which is explained in more detail in appendix B, image cubes and endmembers were created using UV light. Two different excitation sources were used to created the maps in figure 4.3b and d. This showed that the red lakes were indeed present in the lips and flesh tones. Finally, the background also contains indigo, which is explained in section 3.2. RIS was used to determine this as shown in figure 4.4. The 'blue', 'red' and 'aqua' spectra in 4.4c show a sharp increase in reflectance at 705 nm. This is an indication of indigo. These three spectra may be seen as representative for the entire background [7].

An overview of the reconstructions with their ingredients used and the cross-sections they were based on can be seen in table 4.1. The location from which the cross-sections have been taken can be seen in figure 4.5. The pigments of the paint of the lips were based on non-destructive methods only. Wet-in-wet blending with the paint from the white teeth occurred in the painting, therefore the build-up of the lips might not be fully captured by the reconstructions.

Figure 4.5: The locations where cross-sections of *Girl with a Pearl Earring* have been taken. Image obtained from [2].

All paints were made by dripping linseed oil on the dry pigments until a workable paint was reached. Afterwards, they were applied on a black-white opacity chart with a draw-down bar. This is a applicator from stainless steel which has four different sized gaps and makes it possible to create flat layers of paint of a specific thickness [11]. The original layer thickness of the paint was roughly 10-30 μm [3], but the draw down bar could not apply paint that thin. Therefore the reconstructions were made with a thickness of 50 μm. How the paints were applied can be seen in figure 4.6. Samples of the underlayers were also made, but since no lakes were present in those samples it was decided not to use them since the colour would not change in the same way over time. For the background several options of paint compositions were made since the original hue of the colour is unknown. The ratio of the ultramarine and the yellow lake in the glaze layer on the headscarf is decided based upon [11]. The amount of samples made varies from one to four per colour. Those samples were cut into pieces to make so called 'take out' panels. These panels can then be artificially aged for different amounts of time. After a number of hours, one of the take out panels can be extracted from the apparatus while leaving the others. The colour change can then be mapped on various points in the aging process. Both the black and white background are taken into account.

Table 4.1: Location on the painting and the ingredients of the reconstructions Mané made. The numbers refer to the locations of the cross-sections used, which are defined in figure 4.5. For the determination of the contents of the paint for the lips only non-destructive techniques were used.

Rough location	Exact location	Ingredients	Based on
Face	Highlights face	Lead white (Pb) + vermillion (Hg) + few particles of red lake + yellow earth (Fe). There is also a single particle of ultramarine.	#40
	Lips	Vermillion (Hg) + little lead white (Pb) + red lake (K) (American/Mexican cochineal) + earth pigments (Fe) + small amount of ochre	None
Blue headscarf	Glaze layer headscarf	75 % Ultramarine + 25% yellow lake (Ca-chalk)	#41
	Blue layer midtones	Lead white (Pb) + ultramarine	#41
	Blue layer shadows	small amount of lead white (Pb) + ultramarine + yellow lake + little bit of gypsum	#42
Background	Background 70/30	30% Indigo + 70% weld (Ca + Al + K + S) Made in copper pot	#19
	Background 50/50	50% Indigo + 50% weld (Ca + Al + K + S) Made in copper pot	#19
	Background Verdigris	Indigo + weld + verdigris + tiny bit of lead white	#19

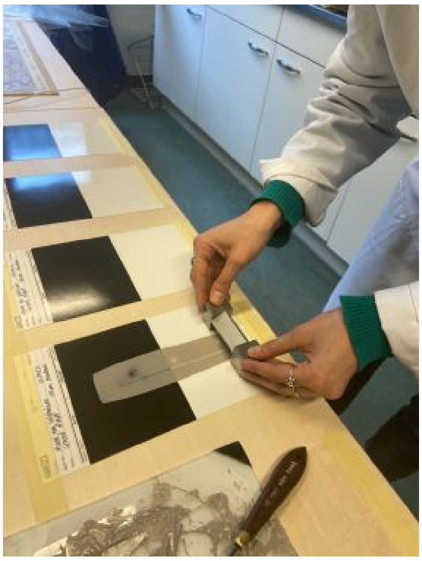


Figure 4.6: Mané is using a draw down bar to apply paint on an opacity chart. Picture made by Abbie Vandivere.

4.4. Artificial aging

Ultraviolet (UV) light consists of high energy photons which cannot be seen with the naked eye. Absorbance of these photons could result in the emission of visible light photons, which is called fluorescence. In art research, UV light is mainly used to look at binding media and varnish. Due to the strong absorbance, the light can cause damage to a painting when the exposure is long [13]. The photons in the light beams will activate the molecules, one molecule for every photon which is absorbed. The energy of every photon will be lost by the molecule due to one of the following causes:

- heat
- emission of radiant energy
- a chemical change of the molecule
- breaking of chemical bonds
- energy transfer to another atom or molecule

This whole process is called primary photochemistry.

Photochemistry in paints is a complex process with a low efficiency. There is no threshold of light intensity, since the energy of the photons is the decisive factor of the photochemical change. This means that photochemical reactions will take place at every light intensity. Therefore, the total amount of damage can be expressed as the product of the illumination times the time. This is called the reciprocity principle [36].

However, there may be some exceptions when the reciprocity principle is not valid, because there are factors which influence this process. These are for example, the oxidation, penetration depth or moisture content [37]. Furthermore, in artificial aging the temperature of the sample may rise due to a high intensity of illumination [36]. Finally, the spectrum of the used light source could be a problem, since the reciprocity principle is historically measured with luxmeters and those do not measure the spectrum. Overall it can only be used if there are no variations in temperature, humidity and spectrum, and not on all materials [38]. Even if the reciprocity principle is valid, there could also be factors that influence the results. Other factors as air pollution can deteriorate the painting as well and is normally not taken into account [37].

In this research project, artificial aging by UV light is conducted using a Q-sun LX-5056 at AkzoNobel in Sassenheim. The samples are put into a fading chamber and are exposed to a Xenon arc lamp with daylight F filters, which provides an excellent simulation of sunlight through window glass [38]. The experiment is conducted under the CIE D65 standard, which is used for indoor paints at AkzoNobel. The temperature was 38 °C and there was a moisture level of 38%. This last parameter is contrary to the standard, however the Q-sun did not work with the required 50%. The irradiance was 0.51 W/(m^2 · nm) at 340 nm. Previous research on artificial aging like [16] stated the illuminance of samples in lux. However, lux is a measure of the response of the human eye to light. In the region where the eye response is nearly zero, the spectral response of most materials, including oil paintings, is high as illustrated in figure 4.8. Therefore lux should not be used to quantify the risk of photodegradation. The energy is thus measured in Watts per square meter. If it is necessary to compare results after all with earlier studies, a value of 8000 lux can be used since this is the illuminance of daylight through a window. This is simulated very well by the Xenon arch lamp [38]. This would say that 48 hour of artificial aging would equivalent to one year of illumination in an museum environment.

An example of how the colours of the reconstruction change can be seen in figure 4.7. The reconstructions that have been aged are shown at the top and their colours are clearly changed with respect to the unaged samples at the bottom. It can be seen that the colours are faded and look pale. The intensity of the colours decreased. The results will be quantified in chapter 6 using the method from section 4.5.

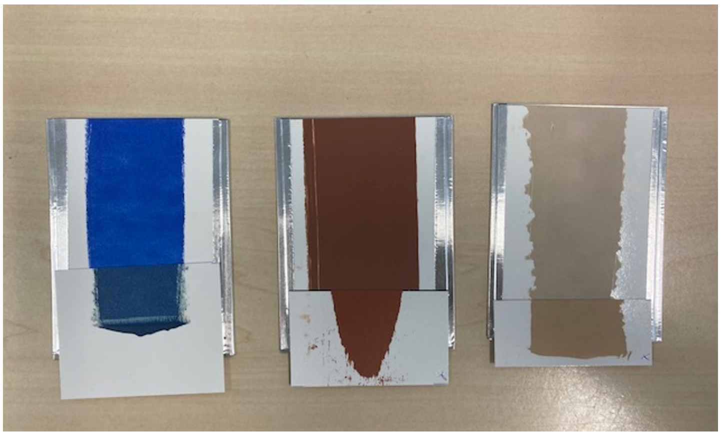


Figure 4.7: An example of how the paint colours are changed after 215 hours. The samples at the bottom show the original colours, the larger samples at the top show the faded colours after 215 hours. From left to right these are the paints of the blue layer shadows, lips and the hghlights of the face. Image taken by Helen Veringmeier-Heemskerk from AkzoNobel.

4.5. Colour measurements

Before, during and after the artificial aging process the colours of the reconstructions have been measured using a BYK-mac at AkzoNobel. These colour measurements include the RGB values, the overall colour change ΔE and the changes in lightness $L*$, redness $a*$ and yellowness $b*$, as explained in section 2.4. One specific take out panel per colour was used for the colour measurements after each artificial aging step. The colour measurements were executed under an angle of 10 °, which is according to the CIE D65 standard.

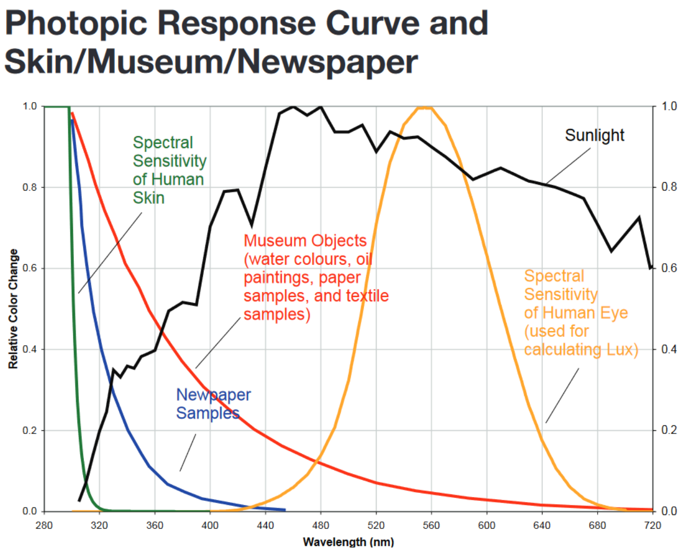


Figure 4.8: The photopic response curve for various materials, with oil paintings indicated in red. Furthermore, the spectral sensitivity of the human eye can be seen in yellow. Image obtained from [38].

4.6. BRDF

After the samples have been artificially aged, they have to be digitized to be able to create a digital reconstruction. To make this realistic, both the varying surface reflectance as the geometry should be captured. RGB values are not enough to fully describe the object since three channels are not enough. Finer sampling should be applied and therefore it is better to use reflectance transformation imaging [39].

This project uses a Total Appearance Capture material scanner (TAC7) to measure multi-spectral images under various light conditions. The geometry data is acquired using four cameras on various inclination angles. They observe Gray code patterns projected onto the surface of the object. It is placed below a hemisphere with 30 LED sources. The surface colours are also acquired by these cameras. Four additional LEDs, white and colourful, are behind rotating spectral filters. Therefore various light and view configurations arise. Images are then made with several exposure times. Afterwards multi-spectral BRDF's can be fitted using this data. Limitations of this method are that approximations have to be made in the geometry and that only small samples fit into the apparatus [39].

A bidirectional reflectance distribution function (BRDF) describes the interaction of light of an opaque surface, depending on incoming and outgoing light directions. From the measured data, the BRDF can be approximated, although it is often possible to fall back on analytical models for this purpose [40], which can describe most isotropic materials reasonably well [41]. Due to its amorphous nature, paint can be assumed to be an isotropic material [42]. Because of the low sampling rate and noise level the final visual result depends heavily on the choice of the model [41]. Section 5.2 describes the various models which are used to create the digital images. Besides its use in cultural heritage, BRDF is also used in special effects in films and by architects and engineers in the process of picking the right material for their projects [40].

5 Models

Computational methods are more and mo re applied for reconstructing artwork. This chapter describes several possibilities of how it can be used. It focuses on the sub question *How can the degradation pattern be digitally reconstructed?* Section 5.1 describes how digital reconstructions have been used in the arts and section 5.2 describes how the images can be rendered.

5.1. Digital reconstructions

The degradation of paint has been described in chapter 3. These changes may affect the colours of the paint largely, but are irreversible and it is therefore impossible to observe the painting as it looked like when it was painted. However, using digital techniques it is possible to make an impression of such a recently finished artwork [43]. Several attempts have been made and will be explained in the next paragraph.

The first example of digital reconstruction without taking samples [44] was the painting of *St. Luke* from Hendrick ter Brugghen suffered greatly from smalt discolouration, as explained in section 3.5. Therefore, the colour was to be reconstructed using information acquired using neutron activation analysis and autoradiography, which uses emitted radiation from the decaying isotopes in the painting. These elements have a high cross section for neutron absorption and a specific half-life time. The beta and/or gamma radiation emitted can be linked to the radioisotope. The gamma radiation shows which elements are present in the painting, but the beta radiation is more useful in this case. When in contact with the source, a photographic film can be blackened by them. This provides an image of the distribution of the elements. Due to the varying decaying times of the isotopes, this should be performed in various time slots after irradiation to show different layers of paint. Finally, the reflectance spectra of undiscoloured smalt was determined and converted to RGB values. The autoradiography of arsenic, which showed the most clear contrast in the smalt distribution, was made into a blue image using the RGB values mentioned before. All data merged together showed the digital reconstruction of the painting [23].

Another example is the reconstruction of the colours of *Field with Irises near Arles* by Vincent van Gogh. The paints which he used were physically reconstructed as realistic as possible. Based on measurements by a spectrophotometer the reflectance spectra were determined for all pigments, which were mixed in varying ratios. They were then used to determine the Kubelka-Munk factors K for absorption and S for scattering, as described in section 4.2. These data allowed the paints to be virtually mixed, which can be used to digitally reconstruct the colours used in the original paintings [35].

There are several complications with the development of digital reconstructions, which should be taken into account. Firstly, it is not always clear how much the material has discoloured when some pigment is still present. Another factor is the change of refractive indices of one of the layers, which can decrease the hiding power of a pigment. This causes increased transparency of the paint layer and therefore the underlaying layer might become visible [23]. Depending on the research method used, the measured intensity signal of a paint layer might be an overestimation since normally mainly the surface pigments

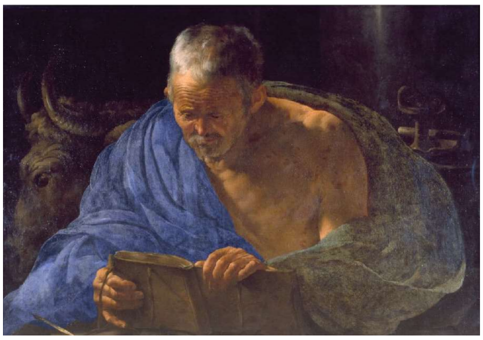


Figure 5.1: The digital reconstruction of *St.Luke* from Hendrick ter Brugghen. The left part of the mantle is reconstructed, the right side is the current state. Image obtained from [44].

influence the colour. Furthermore, some research methods depends on spot samples which shouldn't be taken as representative for a whole layer of a painting [44]. Therefore, a digital reconstruction will always be an approximation of how the painting might have looked since colours depend on many factors like the binding media, added other pigment and transparency of underlying layers [23].

Both projects show that some research was done on the digitally reconstructing of the original paint colours. However, both methods also have drawbacks. Autoradiography, like done on the painting of *St. Luke* can only be done on several elements like manganese, copper and sodium. Pigments like lakes, indigo, chalks and lead white cannot be detected with this method [45]. In *Girl with a Pearl Earring* important causes of discolouration are the fading of lakes and indigo and lead soap formation. Therefore this method is not suitable for this painting. The reconstructed of the mixtures as done on *Field with Irises near Arles* could be applied to *Girl with a Pearl Earring*. However, they did not use the digital colours to reconstruct the painting, only the colours as they came from the paint tubes [35]. The distribution of those paints on the painting should also be taken into account for that. Therefore this method could be useful in a digital reconstruction of *Girl with a Pearl Earring*, but it is not a complete solution.

5.2. Methods of image rendering

To inspect object surfaces, BRDF had been used in the arts [39]. Section 4.6 describes the acquisition process of such data. When computer images are digitally rendered, it is important to determine how the original object interacts with light to ensure a realistic simulation. Images are then generated using reflectance models [46]. This is done by following the rendering equation:

$$L_o(p, \omega_o) = \int_{S^2} f(p, \omega_o, \omega_i) L_i(p, \omega_i) |\cos \theta_i| \, \mathrm{d}\omega i \tag{5.1}$$

which consists of the integration of the incident light L_i at point p coming from direction ωi. The scattering properties are represented in the spatially-varying bidirectional reflectance distribution function $f(p, \omega_o, \omega_i)$ and factor $\cos \theta_i$, which accounts for the influence of light orientation. The result of is the outgoing distribution of light $L_o(p, \omega_o)$. The integral covers the hemisphere relative to the normal vector **n**, as can be seen in figure 5.2.

The scattering data can be analyzed using various models. They all have the tradeoff between realism and efficiency. The models can be compared by the mean squared error between the measured BRDF and a target model. However, this might not be the best visual match, which can be explained by to the dependence on illumination or scene geometry. An example of seven BRDF models models can be seen in figure 5.3. From these the Ashikmin-Sherley, Cook-Torrance and He models would provide the best fit, probably because of their good modeling of the Fresnel effect [41]. This effect states that the reflectivity increases as the angle between the normal and view vector increases [42]. All these models are a linear combination of a specular and diffuse component [46–48]. The specular component is the directly reflected light [46] and the diffuse part comes from the internal scattering of the light rays or from the multiple surface reflections in the case of a rough material [46]. This component is small for

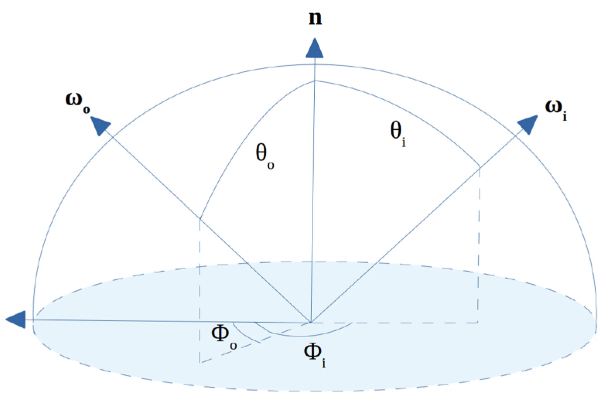


Figure 5.2: The parameters of a BRDF function, showing the incident and outgoing light directions $\omega(\theta, \phi)$ relative to the normal vector **n**. Image obtained from [40].

metallic surfaces, but can be significant for rough surfaces, or which are painted [47]. However, the acquired data is adapted during post-processing. The 3D data are interpolated to create a height map. Therefore, a 2D data set with corresponding height values remains [39]. In that case the Ward model is superior [41] and therefore this is used. This model is described by:

$$\rho(\omega_i, \omega_o) = \frac{k_d}{\pi} + \frac{k_s(\mathbf{h} \bullet \mathbf{h})}{\pi \alpha_x \alpha_y (\mathbf{h} \bullet \mathbf{n})^4} exp - \frac{((\mathbf{h} \bullet \mathbf{x})/\alpha_x)^2 + ((\mathbf{h} \bullet \mathbf{y})/\alpha_y)^2}{(\mathbf{h} \bullet \mathbf{n})^2} \tag{5.2}$$

where **h** is the unnormalized halfway vector between ω_i and ω_o. The estimated parameters are **n**, the surface roughness parameters α_x and α_y and the diffuse and specular albedos k_d and k_s. Firstly, the surface normals are estimated. Then the remaining parameteres are obtained using an initial clustering step. Pixel per pixel a refinement than takes place using several iterations to fully determine them. Then the desired object can be rendered in real-time [39]. Other BRDF models are described in more detail in appendix C.

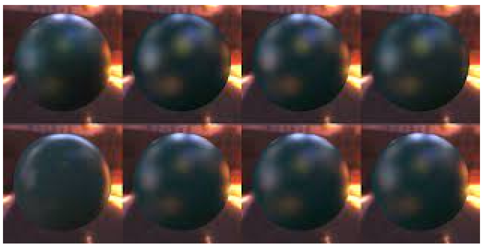


Figure 5.3: A fit of a green-metallic painted sphere with seven BDRF models. Clockwise from the upper left are these: Measured, Ward, Ward-Duer, Blinn-Phong, He, Ashikmin-Shirley, Cook-Torrance and Lafortune. Image obtained from [41].

6

Results

6.1. Results artificial aging and colour quantification

The results of the artificial aging process, as described in section 4.4, will be presented in this chapter. The colour difference ΔE of the paint samples, as explained in equation 2.1 can be seen in figure 6.1, 6.2 and table 6.1. For the white background samples, the colour of the glaze layer in the headscarf and the blue layers in the shadows of the headscarf changed rapidly and reached its maximum quickly. This can also be seen in the table which shows the visual colour change. Only the first step shows a significant colour change. The other blue layer, the layer in the midtones, aged in a slower path. It has a similar aging profile as two of the background samples, namely the verdigris and 50% weld/50% indigo. The sample with 70% weld had a slow start, but reached the largest colour difference of all samples. The flesh and lips samples aged slowly and reached a low colour difference. For the black background, it can be seen that the colour change is overall much lower than on a white background. Only the flesh and lips samples behave similar on the varying background. It takes also more time to reach the maximum colour change. The sample of the blue layers of the headscarf reaches the maximum colour change here, with the sample with 70% weld achieving a relatively low colour change. The sample of the glaze layer of the headscarf also has a slow start, but has the second largest colour change. All other samples change in a moderate path, relatively slow but steady. For two headscarf samples, namely the glaze layer and the one of the shadows, the colour change suddenly starts up again. It is uncertain what caused this effect. A possible explanation could be a secondary reaction that takes place.

The graphs of the change in redness, yellowness and lightness can be seen in appendix A.

Figure A.1 and A.2 show the change in redness a^* in the paint samples. Both graphs show the same, namely the large decrease in redness of the lips and a smaller decrease of the flesh paint. These are the samples with red lakes, which corresponds with the positive starting value on this axis. Furthermore, the samples with yellow lakes all start in with a negative redness. This means that the samples are more green than red. The samples, especially on a white background change colour from green to a more neutral colour value. This is expected to be similar to the behaviour of the original painting.

Figures A.3 and A.4 show the change in yellowness b^* of the paint samples. Especially the glaze layer and blue layer shadows samples of the headscarf change colour here, and again mostly on the white background. These samples decrease in yellowness, and thus become more blue. The other yellow lake samples decrease a bit in yellowness. The lips and flesh samples barely change colour. On the black background, only the two headscarf samples which changed the most on the white background show a colour change here. All other samples barely change.

Figures A.5 and A.6 show the change in lightness L of the paint samples. There is not a lot of change in the lightness. The background samples exhibit the most change, and then mainly the 70% weld/30% indigo sample. The samples with 50% weld changes colour second most. Furthermore, most samples barely change lightness.

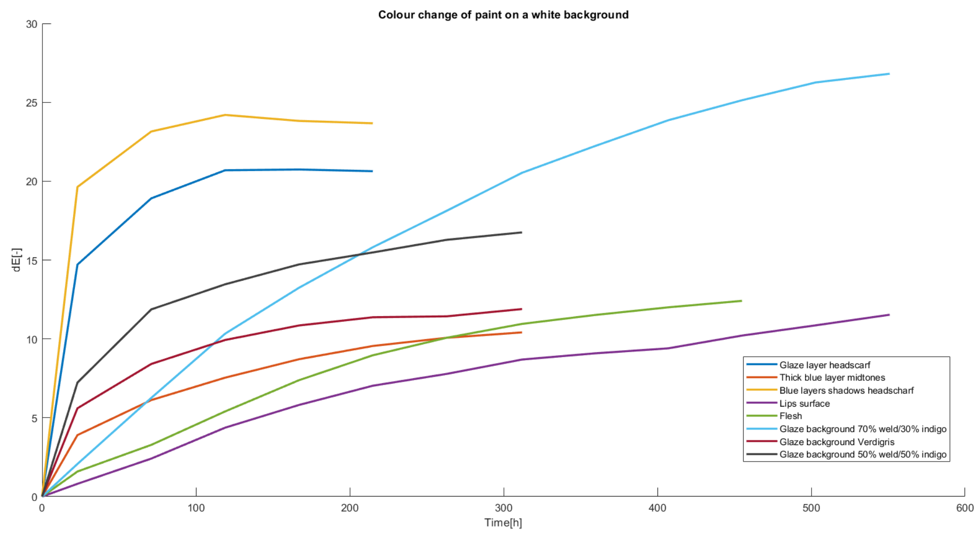


Figure 6.1: The colour change over time of reconstructed paint from *Girl with a Pearl Earring* on a white background due to artificial aging.

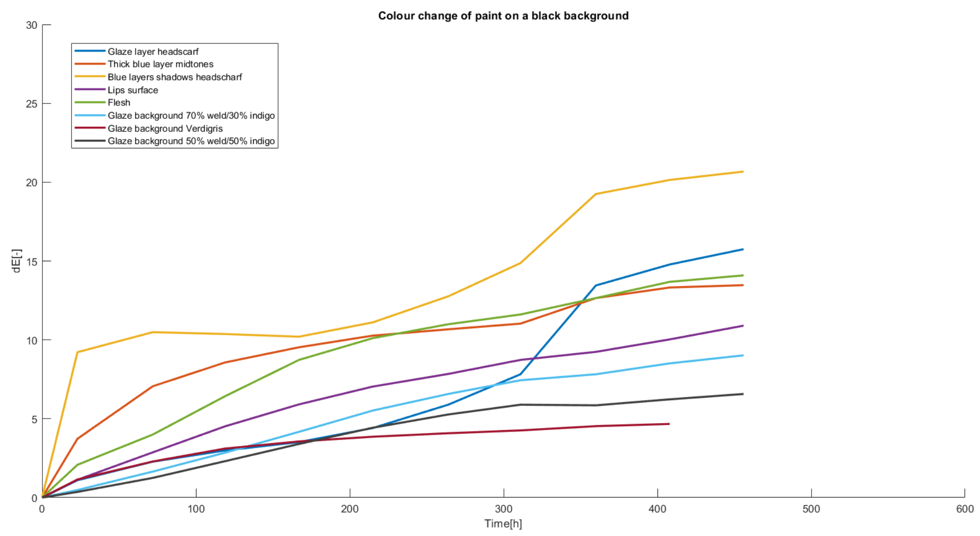


Figure 6.2: The colour change over time of reconstructed paint from *Girl with a Pearl Earring* on a black background due to artificial aging.

Near the end of the artificial aging process, an external calibration was executed on Q-sun. This calibration included the moist function, which caused the panels to get wet. The affected samples are: the longest aged take out panels on the white background, the lips and 70%/30% background; and all panels which were in the machine during the 311-408 hour period with a black background. This means that the panels which were in the machine at that point are not flat anymore, but bubbly like paper which has been wet. However, the colours seem to be unaffected.

Using the method explained in section 4.5 the RGB values of the reconstructed and aged paints are determined. This is compared with the RGB values of the painting in the current state, determined using Paint. Ideally, the original colour of the reconstructions would then tell us how the original painting looks like. However, the RGB values of the painting are problematic to measure. This is because it is difficult to determine the exact location on the painting for every sample and because the RGB values of the colours of the painting vary significantly, due to the paints being mixed and therefore not being there by itself. Furthermore, the reconstructions are not opaque and the background can be seen through the paint. This influences the colour measurements as well. When it was possible, the locations of the cross-sections which were used by Mané to determine the paint composition have been approached. The results of can be seen in table 6.2. It can be seen that for light samples, face and lips, the white background suits better. For the dark samples, the background, the black background samples are a better fit. Note that the contents of the background paints are uncertain, but they are all based on the same location of the original painting. However, overall the differences between the measured RGB values and the RGB values of the painting are large. Therefore this is not a very suitable manner to reconstruct the colours of the original painting. There are too many uncertainties in this method.

6.2. Expected colour change

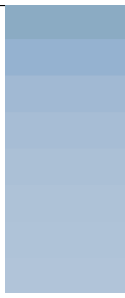
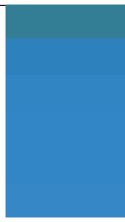
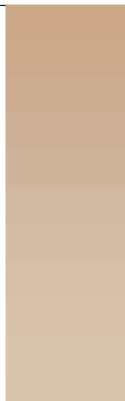
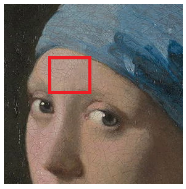
Looking back at section 3.1 and 3.2, overall the results comply to the expected results. However, since no structural or chemical research was done on the reconstructions it is not unambiguously proven that these fading mechanisms apply, it can only be said that the perceived behaviour is what would be expected if these mechanisms occur. This is especially clear in the separate graphs of the change in redness, yellowness and lightness. The samples with red lakes became less red and the blue samples with yellow lakes more red, which means less green. The yellowness decreased in the samples with yellow lakes. And finally, the lightness changes mainly in the background. Looking at the graphs for the overall colour change, the background and the blue part of the headscarf seem to have changed the most in colour. This is a large part of the painting, meaning that a reconstruction of those will have a large influence on the perception. Surprising was the large colour change in first 23 hours for the glaze layer and the shadow reconstructions of the headscarf. It was not expected to happen so fast. It is possible that the paint already discoloured before the first measurements occured. It would be interesting to speed up the process of painting reconstructions and aging to see if this would influence the results. Due to the fast colour change, there are no intermediate measuring steps taken. It would be interesting to add them. The RGB measurements on the non-aged samples by AkzoNobel showed that there were clear differences between the black and white background samples. However, the paint is exactly the same since the opacity sheets were cut in half, so it is clear that the background itself influences the measurements a lot. A reason for this might be that the paint is not applied in an opaque way, the background can be seen clearly through the paint as can be seen in figure 6.3. The RGB values show this as well since for the darker samples the black background values are a better fit to the original painting than the white background values and the other way around. This is a disadvantage for this method, but it also is important for the BRDF acquisition. The background influences those measurements as well.

Figure 6.3: A take out panel before it was artificially aged. The arrow shows that the background can be seen through the paint.

6.3. Results BRDF

To generate the desired images of the painting, the BRDF image rendering method in section 4.6 and 5.2 should be executed. Using the take out panels at various time points in the artificial aging process, it is possible to create an image at several different moments. One of those would be the moment that the painting left Vermeer's studio, which was one of the research topics of the *Girl in the Spotlight* project. The data acquisition has taken place. Only the first and final steps of the colour change have been measured using BRDF equipment. This is because the take out panels have not stopped changing colour when they were taken out of the Q-sun. Therefore all panels have now the same colour and cannot be used anymore to pinpoint steps in the aging process. Using figure 6.1 it might be possible to simulate the behaviour of the colour change. However, the full process takes a lot of time and should be executed by external people. Due to the time constraints on a master's thesis and the dependance on others this step isn't finished yet.

Table 6.1: An overview of the colour change of the white background reconstructions due to artificial aging. The colour at the top is the original colour, the colour at the bottom is the colour after artificial aging. The location of the pigment in the painting is shown as well.

Sample	Hours aged	dE	Visual colour change	Location in painting
Glaze layer headscarf	215	20.63		
Blue layer midtones headscarf	312	10.41		
Blue layer shadows headscarf	215	23.67		
Lips	551	11.53		
Highlights face	455	12.41		

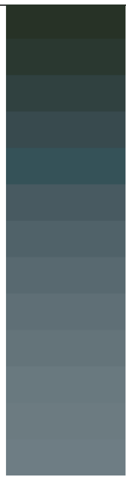
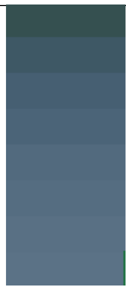
Sample	Hours aged	dE	Visual colour change	Location in painting
Glaze background, 70/30	551	26.81		
Glaze background Verdigris	312	11.89		
Glaze background 50/50	312	16.75		

Table 6.2: The RGB values of the location of the reconstructions in the original painting. Furthermore, the RGB values of the artificially aged samples and their original colour for both the white and black background.

Sample	Current colour original painting	Colour artificially aged reconstruction white background	Original colour reconstruction white background	Colour artificially aged reconstruction black background	Original colour reconstruction black background
Glaze layer headscarf	R33 G81 B110	R0 G118 B195	R19 G116 B158	R49 G74 B99	R35 G40 B44
Thick blue layer midtones headscarf	R92 G127 B149	R177 G196 B217	R139 G171 B195	R186 G203 B219	R142 G166 B185
Blue layer shadows headscarf	R41 G64 B74	R54 G135 B198	R51 G126 B149	R101 G140 B176	R64 G94 B109
Lips	R141 G70 B57	R146 G106 B88	R158 G93 B69	R150 G109 B91	R156 G93 B69
Highlights face	R184 G156 B143	R217 G196 B172	R203 G167 B134	R217 G200 B178	R196 G166 B133
Glaze background, 70/30	R43 G39 B36	R110 G125 B132	R39 G50 B38	R61 G63 B66	R33 G33 B32
Glaze background Verdigris	R43 G39 B36	R78 G104 B108	R69 G90 B73	R55 G57 B58	R40 G41 B39
Glaze background 50/50	R43 G39 B36	R91 G114 B134	R53 G80 B80	R55 G55 B57	R32 G30 B30

7 Discussion

7.1. Reconstruction of the painting

Little research has been done on the combination between physical and digital research methods. However, this collaboration can add new knowledge to *Girl with a Pearl Earring* and other artworks. Without the use of modern day technology, it is not possible to perform optimization like this and reproduce the original of the painting. This research might be a first step, but when the possibilities have been explored more, it can have a lot of impact on the art sector. For example, a neural network could be made when enough paintings have been digitized and Artificial Intelligence could be used to speed up research on similar paintings. But not only that, it can also inspire the common crowd. Especially for artworks like the *Girl* which are widely appreciated by the public.

Figure 7.1 shows a the original painting (a) next to a digitally adjusted version (b). A yellow layer has been added over the regions where it presumably faded away by Elmar Eisemann. It can be seen that the contrast between the face and the background is increased. The edge between them is sharper than in the current painting. This causes a three dimensional effect, the *Girl* is almost coming out of the painting. However, this is only a rough estimate. Firstly because only the yellow lakes have been taken into account. Secondly because the amount of colour change is not quantified. Therefore it is not certain that it looked this way.

Figure 7.1: a) The original painting *Girl with a Pearl Earring*, same as figure 1.1 b) An adjusted *Girl with a Pearl Earring* by Elmar Eisemann (TU Delft), made by adding a yellow layer to the calcium-rich areas.

This is taken a step further. Both points missing from the reconstruction of Eisemann were tackled in this project. Firstly because not only the yellow lakes, but also the red lakes and the indigo will be taken into account. Thereby a large part of the painting is being reconstructed. Secondly, the colour change was measured and quantified. The redness and yellowness decreased, therefore decreasing the colour saturation. This also is true for the background colours, since they became more grey.

Overall, the decreasing contrast between colours next to each other is illustrated in figure 7.2. The original colours of the face and the background, at the top, have a much larger contrast than the aged colours, at the bottom. An image of the painting is created with increased saturation and contrast using Photopea, which can be seen in figure 7.3. To create this, the difference in saturation, lightness and hue is measured between the original paint reconstructions and the artificially aged reconstructions. This is done for the flesh tones, background, blue headscarf and the lips separately. These area's are based on the information obtained with XRF/RIS data which was visualized in 4.3. In chapter 6 it was seen that the colours there were indeed changed during the artificial aging step. For every part, the colour of the aged paint has been adjusted in Photopea to match the original colour of the paint as well as possible. The values of the saturation, lightness and hue needed for this can be seen in table 7.1. Then an overlay on the painting with the new colour is added on top of the flesh tones, lips, blue headscarf and background. Note that this is a very rough way of colour reconstruction. This should not be seen as a final image, but as a first step to visualise the the changes in the paint over time. The image should therefore not be seen on a larger scale. Too many small details would then be visual and this research method is not suitable for that. But on a smaller scale, comparisons can be made between the original painting and the adjusted version.

Figure 7.2: The colour change on the blue glaze layer, lips, flesh and 70/30 background paint. The original colours are at the top, the colours after the final aging step at the bottom. It can be seen that the contrast between the original colours is much greater than between the aged colours.

Table 7.1: The changes made in Photopea to four parts of the painting as seen in figure 7.3. The numbers are based on difference between the original colour of the paint and the colour change due to artificial aging of the paint reconstructions, as seen in Photopea. An overlay with these adjusted values is added to the painting.

Part of the painting	Hue	Lightness	Saturation
Flesh	0	-12	+40
Background	-72	-64	+26
Blue headscarf	-8	-20	-18
Lips	0	-6	+35

Figure 7.3: a) The original painting *Girl with a Pearl Earring*, same as figure 1.1 b) An adjusted *Girl with a Pearl Earring* with increased saturation, hue and lightness according to table 7.1.

7.2. Assumptions

Important assumptions which were made in this research include the paint composition. It is made as close as possible to Vermeers original paint, but it is impossible to copy the ingredients and their ratio exactly after 350 years. This applied especially to the lake components, since they have been degraded. There are indications where they probably would have been present, but there is no way to be certain. The paint used in this research was also made in one batch. For more accurate results it would be better to make several batches of paint and compare the results between them to see if there are differences. Furthermore, the paint layers were thicker than in the original painting because of the draw down bar. It was not possible to make them thinner than 50 μm, while the original paint layers were 10-30 μm.

Another difficulty is the validation of the results. It is of course not possible to replicate aging in paint for 350 years. No large colour changes seemed to occur anymore after the artificial aging process, but it could be possible that some reactions take much more time to take place. Therefore it would be interesting to set up an experiment with a much longer time frame. Due to time constraints of a masters thesis this was not possible for this project.

Since most research on this topic was done with light intensities measured in lux, it is impossible to compare the results. However, using Watts per square meter is a more accurate unit and it should be used instead. An assumption is that 48 hours of aging in this project is comparable to one year of exhibition at a museum environment. This would mean that the time which was simulated during the artificial aging process is 4.8-11.5 years. This seems to be a rather short period of time, especially since most of the colours seem to have reached a steady state. Especially the colours which have been aged the shortest, the glaze and shadow layers of the blue headscarf, are the most stable after the aging process. This would mean that on the original painting, their colour should have changed within a few years. This seems to be very fast. However, unfortunately there is no better information to be more certain about this topic. It would be an interesting topic for future research. Not only the use of Watts per square meter instead of lux, but also the comparison with time passed in the real world. For now, the trends in the colour change can still be studied.
Furthermore, it would be interesting to do chemical research on the aged paints to confirm the expected aging mechanisms. It is now assumed that lakes and indigo faded in the aged paints, which is a reasonable assumption, but it is not proven that it actually happens.

Despite all the points mentioned beforehand, the trends in the colour change were as expected. E.g. the blues of the headscarf became less yellow and the redness of the lips and face samples decreased. This means that maybe the exact values are uncertain, but it can be concluded that the colour change went roughly as this project showed. Since this was the first time that artificial aging has been applied to reconstructions of *Girl with a Pearl Earring* it is an important conclusion.

Furthermore, the colour change in the intermediate take out panels of the reconstructions has continued after they were taken out of the aging equipment. After a couple of months, the panels which were taken out at various times have an equal colour, while the RGB measurements show that this was not always the cause. Apparently the aging mechanisms continues after it is initiated, even if the sample is not illuminated by UV light anymore. If research on this topic is done in the future, it is important that the BRDF measurements on these panels are done in a very short time period after the aging process to prevent erroneous measurements from happening.

It is important to realise that research on artworks as old as *Girl with a Pearl Earring* will always be an assumption. It is simply impossible to exactly recreate all variables needed for a project like this. However, it is also important to validate the information which is known as good as possible. Therefore it is clear that the RGB values obtained differed simply too much from the current values of the original painting. It would be interesting to see how a more advanced method of determining the RGB values of the original painting would look like in combination with more opaque paint samples. Maybe then the results would be more accurate. However, it is not too bad that this did not work out. For the BRDF acquisition it was not possible to use this method since it is not accurate enough and it cannot handle various illumination techniques.

7.3. Perception change and historical context

A clear change between both images is the intense dark colour in the background, which is a large part of the painting. Furthermore, the face is less bland and has a more lively colour instead of pale white. The changes in the blue parts of the headscarf are more subtle, but the colour is darker. Due to the increasing contrast, the edges between the face and the background are sharper and there is a clear three dimensional effect. The *Girl* seems to come out of the page more than in the original painting, she looks more like a real person and looks ready to step out of the image. The colours are more defined instead of patchy and white and the the painting has more life in it. Especially the white collar seems more white, while it did not change in colour. This is because white is a complementary colour to black, as explained in section 2.4. The contrast between the light and dark parts of her face also increased, creating a more nuanced image. This creates also a more three dimensional effect due to adjoining warmer and cooler colours. The lips pop out of the painting due to the more intense red colour. Although less visible, there is also more contrast between the face and the headscarf. A final version of the painting with the appropriate methods would show more contrast and life there as well. As explained in section 3.7 the adjusted painting has more *Houding*, due to the increasing contrast, sharper edges and highlights. It is inviting to scroll through the painting and to keep looking. The original is a more uniform, flat image which is less inviting to have a second look. The use of a camera obscura could still be possible due to the more liveliness and the contrast. It is not proven, but also not invalidated. Of course, this image is still an educated guess, and not a final answer. A more scientific result using the BRDF data would give more information, but how the painting actually looked in 1665 will always be a question.

Nowadays, as *Houding* is not as important anymore, the differences in figure 7.3 are not as upsetting as it would have been for people in the 17th century. It is now normal to see pictures of people and objects, they are not as composed as they were back than. The concept of *Houding* is abandoned, since it is common to see images which do not follow it. Most modern people do not wonder about colour harmony or spatial illusion when they see a image or a painting. Therefore the colour changes in the painting might be less disturbing for people nowadays. However, that does not mean that people can not see the difference when explicitly presented to them. This is why art research is still important to this day.

8

Conclusion

The goal of this project was to simulate the colour change over time of *Girl with a Pearl Earring* from Johannes Vermeer. Using art history knowledge and computational methods this was proven to be possible. The combination of these methods is unique and promising. Data from the *Girl in the Spotlight* project has been extensively used to determine the pigments Vermeer used in the painting.

As a first for the *Girl*, the paints that Vermeer used have been reconstructed and artificially aged. Their colour change was then measured and turned out to be as expected. The mechanisms of indigo, yellow and red lake fading seems plausible. A start in reconstructing the painting has been made by digitally applying these colour changes on the original painting. Such a digital reconstruction using artificial aging data has never been done before. A more scientifically accurate reconstruction is still going to be made using BRDF measurements, which have been executed on the paint reconstructions.

The digital reconstruction showed that the contrast increased and the *Girl* is more lively and looks ready to step out of the painting, there is a clear three dimensional effect. The colours are more defined instead of faded and patchy. More contrast can be seen, which is for example shown in the white collar. It also makes the edges between the face and background sharper. Overall, the painting shows more *Houding* and seems to be more like Vermeer probably intended it to be. The painting in its current state looks more uniform and flat when compared to the digitally reconstructed image. If he used a camera obscura is not confirmed or invalidated. A reconstruction made with BRDF should be more scientifically accurate than the reconstruction presented here. Combining the arts with digital methods is unique and should be explored further in more research. This project proved that it is possible to reconstruct paintings using artificially aging. Paintings can look more like they originally did. This shows us more about the intentions of painters and how people in the 17th century perceived their artworks.

Important points for future research are more opaque samples, which are created in more batches. Another point is that the measured light intensities should not be in lux and to be quick in the BRDF measurements after UV aging. Finally, it would be interesting to reconstruct other paintings, since *Girl with a Pearl Earring* is not the only painting which is discoloured over time. Other paintings from Vermeer or paintings from another painter are interesting to reconstruct as well because it would also be worth knowing to see how they have changed. This project can be the starting point of more and more accurate reconstructions of paintings.

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A

Detailed colour change graphs

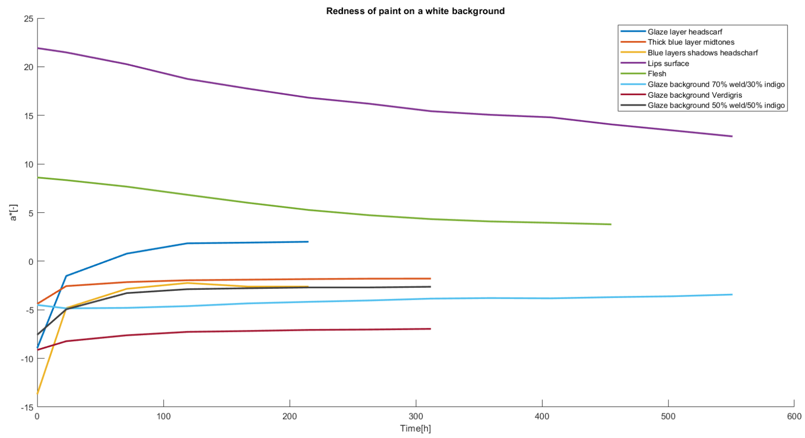

Figure A.1: The change in redness over time of reconstructed paint from *Girl with a Pearl Earring* on a white background due to artificial aging.

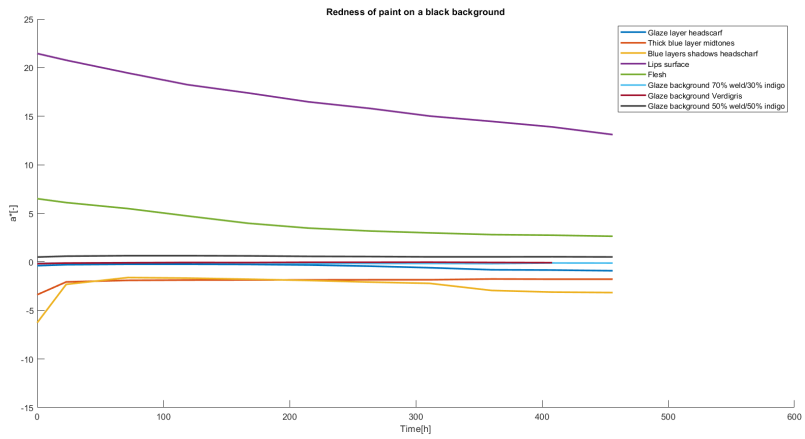

Figure A.2: The change in redness over time of reconstructed paint from *Girl with a Pearl Earring* on a black background due to artificial aging.

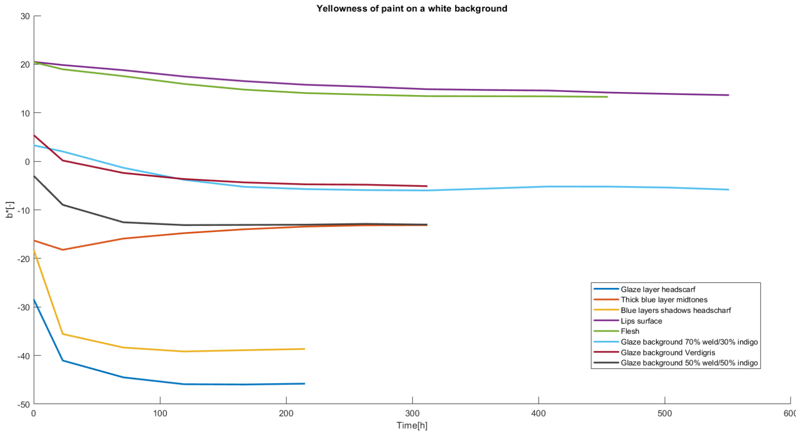

Figure A.3: The change in yellowness over time of reconstructed paint from *Girl with a Pearl Earring* on a white background due to artificial aging.

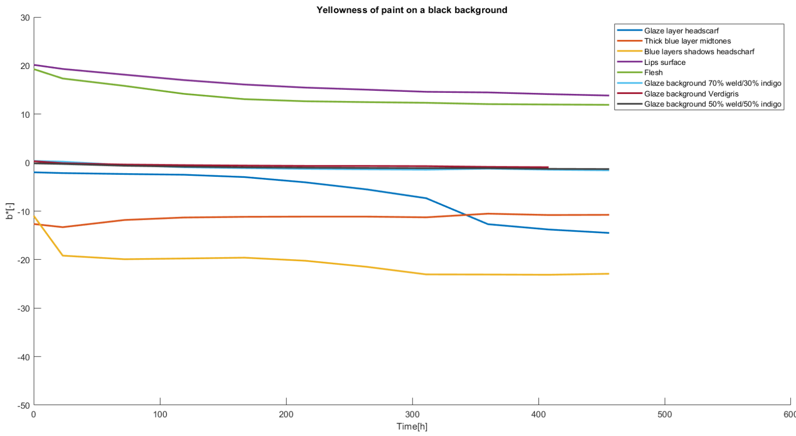

Figure A.4: The change in yellowness over time of reconstructed paint from *Girl with a Pearl Earring* on a black background due to artificial aging.

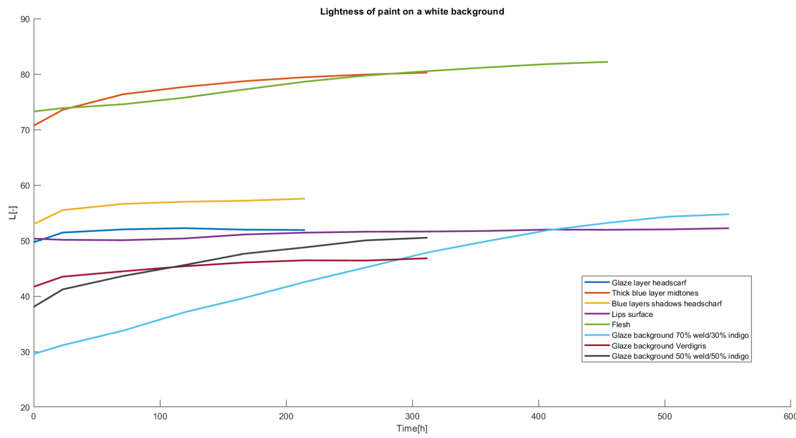

Figure A.5: The change of lightness over time of reconstructed paint from *Girl with a Pearl Earring* on a white background due to artificial aging.

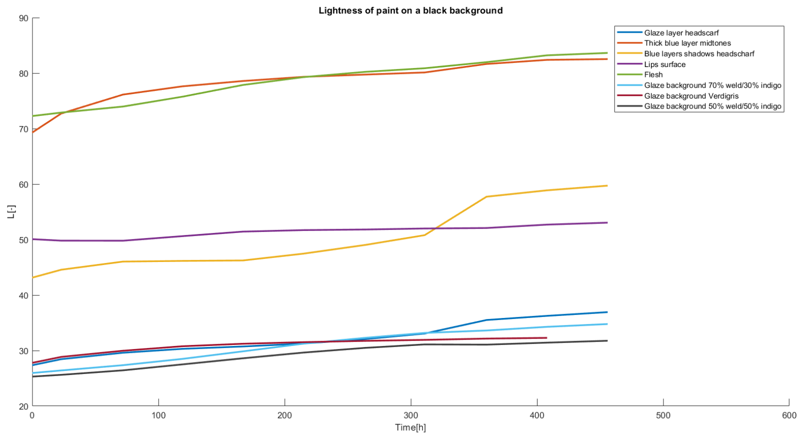

Figure A.6: The change of lightness over time of reconstructed paint from *Girl with a Pearl Earring* on a black background due to artificial aging.

B

Techniques in Art Research

There are various techniques which are used frequently in art research like X-Ray Powder Diffraction or Infrared reflectography (IRR). These techniques are not applied in this project, but will be explained briefly in this section.

B.1. XRPD

X-ray powder diffraction (XRPD) is an x-ray technique which can be split into two different types, namely macroscopic (MA-XRPD) and microscopic (μ-XRPD). Macroscopic diffraction is a non-invasive technique which is applied in a similar way as XRF and those measurements could be acquired simultaneously. MA-XRPD is can visualise crystalline compounds which are close to the surface. Therefore it can be used in art research to visualise degradation products of paint. Amorphous dyes cannot be identified, however, they are often contained in a metallic binder which can be seen in the MA-XRPD measurements. μ-XRPD is an invasive technique which requires the use of samples from a painting. Those samples are used to determine microscopic, chemical information of the paint. The use of samples is a major disadvantage since the painting has to be damaged. Furthermore, it cannot be sure if the conclusions drawn from the sample are representative for a larger area. However, this technique can provide information about all layers of the paint so it proves information about layers below the surface as well. Since each technique has another scale they can be used together to get a full picture of a painting [9].

B.2. IRR

Infrared reflectography (IRR) is a technique which can be used to visualise the underlying layers of a painting [5]. It is used in three spectral bands, namely 1100-1400 nm, 1500-1800 nm and 1900-2500 nm [5]. Using narrow bands can be used to identify different phases of the painting process and to separate pigments from each other within paint layers [6]. Due to a high spatial resolution it its possible to see brushstrokes in lower layers of the painting [6]. A disadvantage of the technique is that several pigments, for example malachite and azurite, cannot be penetrated by infrared radiation. Photons will scatter or be absorbed and therefore it can be difficult to obtain enough details through the paint layers [49]. Also varnishes and binding media can influence the light transmission [49]. Another challenging aspect is the ability to separate the partially penetrated upper layers from the underlayers [6]. A false colour image can be constructed to solve this problem [6]. The three spectral bands correspond to specific colour channels, namely blue for 1100-1400 nm, green for 1500 to 1800 nm and red for 1900-2500 nm [6]. Dark areas in such an image show paint layers that absorb the photons in all the spectral bands and the coloured areas represent paint layers where the absorption changes in per band [6]. Some areas of a painting can appear light due to a thickly applied paint layer [6]. An example of a false colour image can be seen in figure B.1.

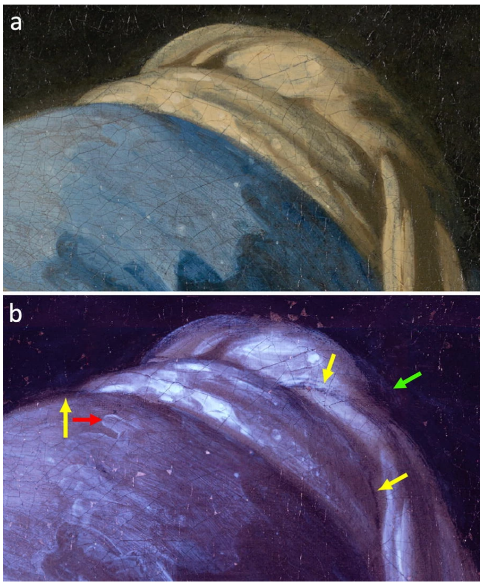

Figure B.1: An example of the use of a false colour image with IRR. a) The visible light photograph and b) the IRR false colour image which shows the brushstrokes in a thick layer (red arrow), black outlines in the underlayer (yellow arrows) and overlapping paint layers (green arrow). Image obtained from [6].

B.3. UV techniques

Ultraviolet (UV) light consists of high energy photons which cannot be seen with the naked eye. Absorbance of these photons could result in the emission of visible light photons, which is called fluorescence. In art research, UV light is mainly used to look at binding media and varnish. Due to the strong absorbance, the light can cause damage to a painting when the exposure is long [13]. The UV-techniques FORS and FIS will be discussed in this section.

B.3.1. FORS

Fibre optic reflectance spectroscopy (FORS) is a technique which is mainly used to detect red lakes in paintings. It is a non-invasive and sensitive technique which uses UV radiation [50]. The radiation is transmitted trough a a fiber-optic probe which results in reflectance spectra that can be processed using the KM theory [51], which was explained in subsection **??**. FORS data can sometimes be used to identify the red lake type [50] or to determine the rate of fading [51].

B.3.2. FIS

Fluorescence Image Spectroscopy (FIS) is a more direct technique to study red lakes in paintings. Using a standard UV lamp it can show excited lake pigments, aged varnish, binding media and other degradation media. However, if special filters are applied, the wavelengths of the light can be limited to excite only the desired pigments. As an example, for red lakes, these are 460-532 nm, which results in fluorescence image cubes with emission maxima at 600-620 nm. Using the data from the image cubes it is possible to make molecular fluorescence maps [7]. An example of the use of FIS in *Girl with a Pearl Earring* can be seen in figure B.2. It can be seen that the red lakes are mainly used in the lips.

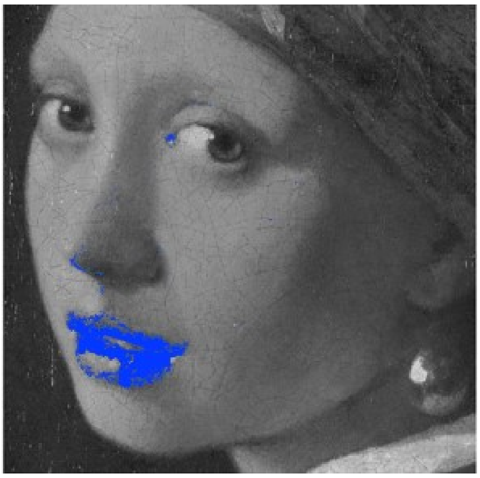

Figure B.2: An example of the use of FIS. It shows red lake fluorescence, which is obtained using UV light. Image obtained from [7].

B.4. Microscopy techniques

The techniques described in the previous sections are all techniques which are used on surfaces, but that is not the only type of research done on paintings. Microscopy is used to investigate samples which were taken from the painting. This section describes the ligth microscopy and SEM-EDX methods.

B.4.1. Light microscopy

Light microscopes are used to enlarge nearby objects. It uses an objective lens with a short focal length with and an eyepiece lens to magnify the image further. The total magnification is obtained by multiplying the separate magnifications of the lenses and can be up to 2000x. The maximum resolution of a light microscope is about 0.2-0.5 μ [42]. Research microscopes can combine imaging with 3D topographic information. This type of microscopes are used on full paintings to show the surface topography and individual brushstrokes [5]. Furthermore, the layering of the paint cross-sections can be seen with light microscopy. Bright field, dark field and ultraviolet are all used in sample analysis [6]. Examples of an image obtained using light microscopy can be seen in figure B.3a and b.

B.4.2. SEM-EDX

A method which can provide more detailed information about the samples than light microscopy is scanning electron microscopy - energy dispersive x-ray analysis (SEM-EDX). For this method, an EDX system is coupled to a scanning electron microscope (SEM). A SEM produces images using backscattering electrons and x-rays are used to determine the elemental composition of the samples [3]. In a low-vacuum system, SEM-EDX can show the layer build-up of a sample and can detect the differences in chemical compositions in various areas of paint. Also the processes of paint degradation can be seen here. High-vacuum systems are more precise in mapping the elements within cross-sections. However samples needed to be coated with carbon before they can be analysed [5]. Examples of an image obtained using SEM-EDX can be seen in figure B.3c and d.

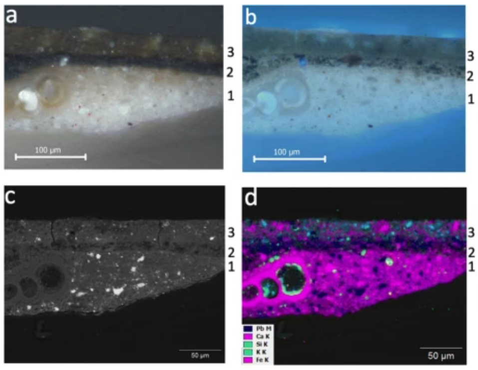

Figure B.3: A cross-section from the lower right background of *Girl with a Pearl Earring*. Picture made with a) light microscope, bright field b) light microscope, UV fluorescence c) SEM backscattering and d) SEM-EDX. Image obtained from [3].

C
More BRDF models

Several BRDF models which were not described in section 5.2 are explained in the sections below.

C.1. The Ashikmin-Shirley model

The Ashikmin-Shirley model focuses on 'common' surfaces and attempts to fulfill the following characteristics:

1. Plausible: this means that the BDRF applies energy conservation and reciprocity
2. Anisotropy: simple anisotropy should be modeled
3. Intuitive parameters: only four parameters necessary
4. Fresnel behaviour: a decrease in incident angle means an increase in the specularity.
5. Non-Lambertian diffuse term: if not, the energy conservation would be violated in case of Fresnel behaviour
6. Monte Carlo friendliness: which would make the model more straightforward to use

Furthermore, the hemispherical reflection is restricted by the addition of some correction terms. The parameters of this model are defined in figure C.1 and table C.1.

For the specular part of the BRDF, the Neumann and Neumann model is taken as a starting point. In this model, the dot product between the unit vector in the reflection direction of the light $\mathbf{r}_1$ and the normalized vector $\mathbf{k}_2$ to the viewer is taken. Then it is raised to the power *n*, which is called the Phong exponent. A perfect mirror is represented by the limit of $n \to \infty$. In the Ashikmin-Shirley model, the Phong parameter is altered into two values. The factor *n* is changed into $n_u cos^2\phi + n_v sin^2\phi$. ϕ Is the angle between the perpendicular projections of the normal and the vector **h** which is half between in incoming and outgoing light beams $\mathbf{k}_1$ and $\mathbf{k}_2$. Furthermore, the microfacet probability density function is added, which models the surface like a collection of small facets of every representing surface.

Table C.1: The definition the parameters in the Ashikmin-Shirley model, also defined in image 5.2.

Parameter	Explanation
$\mathbf{k}_1$	Normalized vector to light
$\mathbf{k}_2$	Normalized vector to viewer
n	Surface normal
$\rho(\mathbf{k}_1,\mathbf{k}_2)$	BRDF
h	Normalized half-vector between $\mathbf{k}_1$ and $\mathbf{k}_2$.
F	Fresnel reflectance

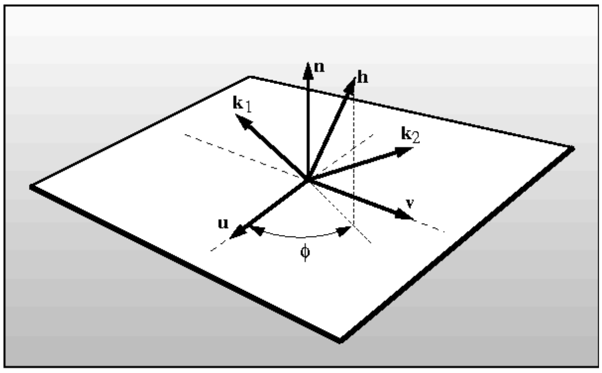

Figure C.1: The geometry of various vectors in the Ashikmin-Shirley model. Image obtained from [48].

Furthermore, energy conservation is implemented. Overall, the specular BRDF of the Ashikmin-Shirley model is calculated as:

$$\rho(\mathbf{k}_1, \mathbf{k}_2) = \frac{\sqrt{(n_u+1)(n_v+1)}}{8\pi} \frac{(\mathbf{nh})^{n_u cos^2\phi + n_v sin^2\phi}}{(\mathbf{hk}) max((\mathbf{nk}_1, \mathbf{nk}_2))} F((\mathbf{kh})) \tag{C.1}$$

where F is the Fresnel reflectance.

An important part of the diffuse solution of the Ashikmin-Shirley model is the behaviour near the grazing angle. The specular reflection is then close to one, making the diffuse colour disappear. However, this is not possible to describe using a common Lambertian term. Another important aspect is the conservation of energy. The total diffuse term is:

$$\rho_d(\mathbf{k}_1, \mathbf{k}_2) = \frac{28R_d}{23\pi}(1-R_s)\left(1-\left(1-\frac{\mathbf{nk}_1}{2}\right)^5\right)\left(1-\left(1-\frac{\mathbf{nk}_2}{2}\right)^5\right) \tag{C.2}$$

By adding the specular and diffuse terms the full BRDF is obtained [48].

C.2. The CookTorrance Model

The CookTorrance model is aimed at being general model for rough surfaces. It can be used for many materials, surface conditions and lighting options.

One assumption of the model is that the ambient illumination is independent of the viewing direction and uniformly incident. Also it is assumed that no nearby objects block the light. This results in the following model:

$$I_r = I_{ia}R_a + \sum_l I_{il}\,(\mathbf{N}\cdot\mathbf{L}_l)\, d\omega_{il}\,(sR_s + dR_d) \tag{C.3}$$

where the sum of all reflected intensities from all light sources is added to the reflection illumination of the ambient illumination. The ambient term is assumed to be uniformly indecent. The parameters of the model are explained in table C.2.

For a reflectance of a smooth surface, the extinction coefficient and the refraction index vary with wavelength. The CookTorrance model uses the Fresnel equation in this case if these parameters of the surface are known. If not, the Fresnel equation is fitted to the measured reflectance of a polished surface. For non-metals, this gives an indication of the refraction index. This dependency also means that the colour of the reflected beam may change. For an incident angle of $\pi/2$ the reflected colour approaches the light source colour. Using interpolation between the incidence angles of zero and $\pi/2$ the colour shift can be approximated. To calculate the exact colour shift would be too computationally expensive.

Table C.2: The parameters which are used in the CookTorrance model [46].

Parameter	Explanation
I_r	intensity of reflected light
I_{ia}	intensity of the incident ambient light
I_{il}	intensity of the incident light
R_a	ambient reflectance
R_s	specular reflectance
R_d	diffuse reflectance
N	Unit normal of the surface
L	Unit vector of the light direction
dω_{il}	solid angle of the illuminating beam
s	fraction of reflected light that is specular
d	fraction of reflected light that is diffuse

Non-homogeneous materials like plastics or paint may have different coloured specular and diffuse components because the colour change might be a result from the surface reflectance only.

Using the spectral energy distribution of the reflected light and the trichromatic colour laws it is possible to calculate the RGB colours on the computer screen [46].

C.3. The He model

The CookTorrance model is aimed at rough surfaces and is not suitable at all circumstances. Therefore, the model is extended into the He model, which can be used for a decreasing surface roughness as well. Furthermore, polarization and spectral dependence are added in the He model.

The improvements of this model are:

- All polarization states are permitted
- All surface types are possible
- Only the illuminated parts of the surface are used in the model

All these factors cause a relatively complicated model. Therefore it is simplified by the approximation via a local tangent-plane and assume that the slopes are gentle.

The total BRDF can be split in three functions, namely a the specular, directional and uniform-diffuse part. The specular function is:

$$\rho_{bd,sp} = \frac{|F|^2 \cdot e^{-g} \cdot S}{\cos\theta_i d\omega_i} \cdot \Delta \approx \frac{|F|^2}{\cos\theta_i d\omega_i} \quad \text{(C.4)}$$

All parameters are explained in table C.3. As can bee seen the specular contribution is proportional to the Fresnel reflectivity. In the limit, for a smooth surface, g →0 and S →1, which means that the specular term is not attenuated. Then the approximation stated in equation C.4 may be used.

The directional diffuse component describes the diffraction and interference effects on the first reflection. The field may have a directional character, but is diffused to the hemisphere. The full equation can be seen in [47]. When the projected size or the surface roughness elements are larger than the wavelength, the directional diffuse component approaches zero.

The uniform diffuse contribution on the BRDF is:

$$\rho_{bd,ud} = a(\lambda) \quad \text{(C.5)}$$

which is a theoretically or experimentally estimated parameter which depends on the wavelength of the incoming light. It can, for example, be calculated from measured hemispherical reflectivities and should be tabulated to be used [47].

Table C.3: The parameters which are used in the He model [47].

Parameter	Explanation
$\rho_{bd,sp}$	specular reflectivity
$\rho_{bd,dd}$	directional diffuse reflectivity
$\rho_{bd,ud}$	uniform-diffuse reflectivity
$\lvert F\rvert^2$	Fresnel reflectivity
g	function of the surface-roughness
S	shadowing function
θ_i	incident energy on polar angle
ω_i	incident energy on solid angle
Δ	delta function
a	uniform diffuse component
λ	wavelength