Virtual reconstruction of hidden paintings based on XRF images

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They are ill discoverers that think there is no land, when they can see nothing but sea.

Sir Francis Bacon
English author, courtier and philosopher (1561 - 1626)
Preface

Three and a half years ago I started with the Master programme Media and Knowledge Engineering. I had decided to take it a bit more slowly and spent some time on extra courses and other projects. I was looking forward to my graduation project, which I would choose such that it would fit perfectly with my interests.

Of course it was not as easy as I thought to find a suitable project. I preferred to graduate at a company to gain some practical experience but most companies did not have what I was looking for. In the end, my search brought me back to Delft University of Technology where a very interesting assignment was waiting for me.

The assignment concerned investigating the use of digital image processing on imagery of hidden paintings. In the summer of 2008 an international research team including members from the 3ME faculty of Delft University of Technology had visualized a lost painting by Van Gogh and the question was whether the imagery could be enhanced with image processing techniques.

The topic of my graduation project thus became virtual reconstruction of hidden paintings, using X-Ray based imagery. And now, one year later, my work is done and the report is written. It describes a promising methodology and discusses the main difficulties.

Since it concerns a graduation project, this report is mostly meant for the graduation commission and supervisor. However, anyone interested in new developments in art restoration is invited to read this report as well.

The reconstruction process has been divided into two stages. Readers interested in finding the hidden painting’s composition in the X-Ray based images are directed to chapter 4. Chapter 5 is of interest when looking for information on how the virtual reconstruction is provided with colour.

Given the multidisciplinary character of the study, some terms from the field of Computer Science may be new to art experts while the artistic aspects may be unfamiliar to computer scientists. In most cases the terms are explained as they appear but a glossary is added as well such that they can be looked up more easily. The glossary also holds explanations of most abbreviations.

Finally, I would like to thank my supervisor Dr.ir. Jan van der Lubbe for his support and guidance. I had a great time working with him. I also would like to thank Dr. Joris Dik for his explanations about the chemical and artistic processes that are involved, and Dr. Emile Hendriks for his ideas regarding the image processing issues.

Last but not least, I would like to thank my boyfriend and my parents. They were not only a great mental support but were also willing to give their opinion on the content of my work.

Delft, December 16th 2009

Marije Nieuwenhuizen

\footnote{Dik et al. [10]}
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Summary

Hidden paintings are very common in the field of art: art historians estimate that one of the five paintings contains a buried composition. Retrieving those hidden layers by scraping off the top layer is generally not an option. For this reason, virtual reconstruction should be studied. Without such methods, hidden paintings might never become visible. This would be a loss since they are often great art historical value.

The main objective of this thesis is to investigate how a virtual colour reconstruction of a hidden painting can be obtained from imagery produced by an X-Ray based method called X-Ray Fluorescence Spectroscopy (XRF). With this technique the chemical elements of the painting can be visualized and a recent study has shown that these visualizations can give a clear view of the hidden painting [10].

Until now, virtual reconstruction of hidden paintings based on XRF images has not been studied yet. The main objective of this study is therefore to obtain a general approach that can be used as starting point for further research.

The XRF technique is frequently applied on paintings to analyse specific points. It offers insight into the chemical composition of the paint at those locations. This knowledge can help identify the pigments that the artist has used which is valuable information for art historians and conservation experts.

XRF can also be used to analyse entire regions of the painting. The produced XRF images (XRFs) are then visualizations of chemical elements: each XRF shows in what concentration a certain chemical element is present at each point of the analysed region. When the hidden painting contains chemical elements that are not or differently used in the surface painting, the XRF images of these elements may show the composition of the buried layer.

In this study, the virtual reconstruction is divided into two stages. First, XRFs of only the hidden painting are obtained. Such a step is necessary since the original XRFs are mixtures of the chemical elements present in all layers of the painting. In the second stage colour is added: the original XRFs are in greyscale which means that some form of colourization is required.

The first step, obtaining the XRFs of the hidden painting, is performed using object matching and inpainting. Based on greyscale values objects are discerned in the XRFs and colour is used to find objects in the image of the surface painting. Then, all XRF and surface layer objects are compared: the similarities between the objects found in an XRF and the objects of the surface painting are computed.

When the similarity between an XRF-object and a surface painting object is above a certain threshold, the pixels of the XRF-object are said to correspond to the surface layer rather than the hidden layer. This means that these pixels should not be used in the reconstruction process.

Leaving out the surface painting pixels causes the XRF images to have 'holes': areas where no information is available. To fill in the missing regions, inpainting is applied. This algorithm (proposed by Criminisi et al. [8]) reconstructs the holes by copying pixels from the remaining image.

The second step, providing the virtual reconstruction with colour information, is performed using an example image. The chemical data provided by the XRF images does relate to the
colours of the pixels but a direct translation is practically impossible. Therefore, some other source is needed for the colour information and an example image is often available. An art expert should provide an image that is likely to contain the same colours as the hidden painting.

The colours of the example painting need to be expressed in terms of the same chemical elements as represented by the XRFs. This can be done using XRF point measurements such that the chemical composition of a selected group of pixels is obtained. The chemical values of the pixels of the example can also be estimated: this method is used in this study.

The example data is used to ‘learn’ which chemical composition corresponds to which colour. More formally, a classifier is trained such that it can classify the pixels of the actual XRF data into certain classes, based on their chemical compositions.

As a classifier, the nearest-neighbour approach is used. The chemical composition of each pixel is compared to the known chemical compositions of the example. The classifier assigns the colour that appears most frequent among the example compositions that match best with the new composition.

Quantitative and qualitative evaluation (using visual inspection) indicates that the presented methods, when combined together, are able to obtain a virtual colour reconstruction of a hidden painting. The procedure has been applied on data of the painting *Patch of Grass* by Vincent Van Gogh and the colours and composition of the produced reconstruction correspond with what is expected.

**Future research** may address several issues. Each of the steps of the described method could be examined in more detail. For example, future research may look into partial matching methods for the detection of surface painting regions in the XRF or experiment with other inpainting algorithms to fill in the missing areas.

Important issues of the colourization process to address in future research are the acquisition of training data and classifier design. Research should investigate the use of XRF point measurements in more detail for example and experiment with other classifiers.

In this study, an example image is used to provide the virtual reconstruction with colour since the colours are highly difficult to determine (if at all) based on XRFs alone. Future research may address this issue more thoroughly however, by cooperating with more experts (especially from the field of art and/or chemistry).
1 Introduction: research overview

This chapter presents an overview of the thesis research. First, the problem addressed in this study is described in section 1.1 along with the research objective. Section 1.2 describes the approach used to achieve the objective and section 1.3 discusses the scope. Finally, the structure of the thesis report is given in section 1.4.

1.1 Research objective

Experts have estimated that approximately twenty percent of all paintings, including Old Master pieces, have other paintings buried beneath their surfaces. These hidden paintings could be revealed by removing the upper layer but in general this is not an option. It is therefore necessary to investigate virtual reconstruction of hidden paintings.

A technique recently applied to paintings, X-Ray Fluorescence Spectroscopy, can produce images that give a good impression of the hidden painting [10](see figure 1.1). Although these images were made at a special facility, the application of portable XRF is now amongst the standard techniques for characterization of elements in painted works of art [35]. For these reasons, the study of virtual reconstruction should be focused on using XRF images.

![Figure 1.1: Image A shows the painting Patch of Grass by Vincent van Gogh. The red frame indicates the region that is scanned with XRF: the amounts of mercury and antimony are given by the XRF images B and C respectively.](image)

Until now no method exists that obtains a colour reconstruction of a hidden painting based on XRF images. Dik et al. [10] has provided a starting point by showing a colour visualization¹ of chemical elements. They use it as an illustration however and do not investigate the reconstruction process itself.

The research of Dik et al. is addressed in more detail in chapter 3, as well as three other studies that look into retrieving hidden layers. Although they are interesting, neither of the proposed methods can be used to obtain a colour reconstruction of a hidden painting.

Without a method to obtain a virtual reconstruction, a lot of valuable paintings remain buried. This would be a loss since they are often of equal, if not greater art historical value than the surface paintings. They can also provide insight into the artist’s working methods or artistic ideas.

¹A visualization is merely making data visible; the term reconstruction is used to indicate that the data is processed and interpreted to obtain an image.
The **research objective** of this thesis is therefore:

> Develop a method that uses XRF images to produce a virtual colour reconstruction of a hidden painting in such a way that the reconstruction contains colours that, according to art experts, are consistent with the real hidden painting.

Throughout this study, the XRF images made by Dik et al. [10] are used to illustrate the described methods. Although there are no other XRF images available (yet), the aim of this study is to develop a *generic* method for virtual reconstruction of hidden paintings.

The lack of examples makes it difficult to ensure good results on other paintings but all approaches are chosen such that they should work on other paintings as well. For example, the proposed methods are not based on characteristics that are typical for the Van Gogh painting.

### 1.2 Research methodology

To achieve the main research goal, two processes are studied. First of all, the original XRF images of a painting with a hidden layer are mixtures of all layers contained in the painting. If such XRFs were used directly, the resulting image would be a mixture of paintings instead of an image of the hidden painting. This means that some separating procedure is required.

Secondly, the XRF images are still in greyscale and to obtain a colour reconstruction of a hidden painting, colour has to be added in some way. This indicates that a colourization step is needed as well.

Therefore, the approach used in this study to achieve the research objective is to divide the main goal into two subgoals:

1. *Develop a method that can obtain XRF images of only the hidden layer of a painting.*

2. *Develop a method that can construct a colour image of a painting that is represented by a number of XRF images.*

The methodology applied to achieve the sub goals is addressed in section 4.1 and 5.1 respectively. A brief summary is given below as well as a graphical overview (figure 1.2).

The methodology used for the first subgoal consists of three main steps. First, objects from both the XRFs and the surface painting are retrieved. In the second step these are compared to find XRF-objects that closely resemble an object of the surface painting. When the similarity is above a certain threshold, the XRF-object is said to belong to the surface painting rather than the hidden layer. Subsequently, the pixels of the XRF-object in question are removed. The holes that are left are reconstructed in step three using an inpainting algorithm.

For the second subgoal a two-step methodology is studied. First, an example image is used to train a classifier to learn which chemical compositions should be linked to which colours. This is done by expressing the colours in terms of the chemical elements represented by the XRF images. In the second step the classifier is applied to XRF data of a hidden painting: it assigns each pixel to a certain class based on the pixel’s chemical composition. Since each class corresponds to a colour of the example image, the pixels are effectively colourized.
1.3 Scope of research

The paintings that are qualified as ‘hidden painting’ are paintings that are fully covered by another painting such that they aren’t visible to the naked eye any more. The painting that covers the hidden one and that is visible to the naked eye, is called ‘surface painting’.

Until now, virtual reconstruction of hidden paintings based on XRF images has not been studied and it is therefore important to obtain a general approach that can be used as starting point for further research. This study therefore focuses on investigating the entire process rather than finding the optimal intermediate steps. Each step is currently implemented such that it illustrates its function; they can be improved in future research.

This study has a multidisciplinary character: fields of interests are mostly art, chemistry and computer science. Although aspects of all three areas play a role in the research, the point of view is mainly that of computer science.

This is particularly important for the colourization process, where some artistic and chemical knowledge is required. This information should be submitted by an expert: this study does not elaborate on the artistic and/or chemical interpretations.

The data on which the reconstruction method is applied, consists of XRF images and an image of the surface painting. The XRF images often correspond to only a part of the surface painting: in most cases a certain region of the painting is scanned and the XRF maps thus show only the elements of this region of the painting.

In this study it is assumed that the image of the surface painting is already cut out to correspond with the region shown by the XRFs. Moreover, it is assumed that the images are registered, either manually or automatically. This means that a pixel at location $P$ in the XRF image corresponds with the pixel at location $P$ in the image of the surface painting.
1.4 Report structure

This thesis report has the following structure:

Chapter 2 gives background information on the analysis technique that is of special interest in this study: X-Ray Fluorescence Spectroscopy. The technique itself as well as applications found in literature are discussed.

Chapter 3 presents an overview of the current state of research on the topic of this study, virtual reconstruction of hidden paintings using XRF images.

Chapter 4 addresses the first stage of the reconstruction method: an object matching and inpainting procedure that can obtain XRF images of only a hidden painting.

Chapter 5 discusses the second stage of the reconstruction method: it shows how a colour image is constructed from an XRF image and an example, using classification.

Chapter 6 presents the conclusions of the research as well as an overall discussion with suggestions for future research.

The Glossary explains the technical terms that may be unfamiliar to the reader. Many abbreviations that are used are described as well.

Appendix A shows how the literature presented in section 2.3 and chapter 3 is found using keyword searches in a scientific database.

Appendix B is added to provide background information on painting and pigments. A number of important pigments are described including their chemical composition.
2 X-Ray Fluorescence Spectroscopy

This chapter provides background information on X-Ray Fluorescence Spectroscopy (XRF): the technique that produces the images that will be used for the reconstruction of a hidden painting. It is a technique that is nowadays frequently used for art analysis.

Given the chemical character of this chapter, the information seems to be beyond the scope of this research. However, it is important to understand the nature of the images used for the virtual reconstruction. This chapter therefore covers the most important aspects and directs readers for further details to sources as [1] and [24].

Section 2.1 starts by explaining the chemical background of XRF. The images that are constructed with XRF are addressed in section 2.2. Finally, section 2.3 presents applications of XRF found in literature to give an impression of the use of XRF.

2.1 Chemical background

Development of electronics in recent decades has brought new analytical instruments, one of which is X-Ray Fluorescence Spectroscopy (XRF) [29]. This technique is used to examine the chemical composition of all kinds of samples.

A recent study [10] (see chapter 3) has shown that XRF is able to visualize a hidden layer more clearly than X-Radiography (XR) and Infrared Reflectography (IR). These are the two most often applied analysis techniques on paintings [20].

X-Radiography is also commonly used in hospitals: an X-Ray beam is shot through the sample and wherever the X-Rays penetrate through all layers, the photographic plate behind the sample will be blackened. Infrared Reflectography records the infrared light that an object emits using a camera adapted to receive infrared radiation.

Although both techniques have their uses, their images do not always provide a clear view on the paint layer hidden beneath the surface painting. For example, if a painting was covered with a basis of Lead White before the surface painting was painted, X-Radiography cannot visualize the buried layer very clearly because the ground layer will absorb all the X-Rays. Infrared Reflectography has a similar shortcoming: the infrared radiation from the hidden painting is too weak to reach through the upper paint layers.

Figure 2.1 presents a very simplified graphical overview of the XRF technique. The starting point is a small X-Ray beam that is shot through a specific point of the sample. If the energy is high enough, some electrons of the atoms that are hit may be expelled from their orbital. This causes the electronic structure of the atom to become unstable, and electrons in higher orbitals 'fall' into the lower orbital to fill in the hole left behind.

The size and strength of the X-Ray beams depends on the source that is used. Sealed X-ray tubes and radioactive sources are most commonly used but X-rays can also be produced in synchrotron radiation facilities. The latter has the advantage that the beam is very precise (0.5x0.5 mm2) and powerful (38.5 keV).

There are a limited number of ways in which the electrons of an atom can fall from their orbital. The main transitions are K-alpha and beta and L-alpha and beta (see figure 2.2). Each
Chapter 2: X-Ray Fluorescence Spectroscopy

Figure 2.1: Graphical overview of X-Ray Fluorescence Spectroscopy. The atoms that are hit by the X-Ray beam may react by emitting energy. These energies can be used to deduce which chemical elements are present at the targeted location.

of the electron transitions yields a fluorescent photon of which the voltage is unique for each element. For example, the K-alpha transition of lead yields a different voltage of energy than the K-alpha transition of mercury. In addition, the K-alpha transition of lead also yields a different voltage than the L-alpha transition of lead.

This means that when the energy emitted by a targeted point is recorded, the detected voltages can reveal which chemical elements are present at that location.

Figure 2.2: Graphical overview of the electron transitions between the shells of an atom.

When the emitted energy of a targeted point is recorded, an energy spectrum is acquired (an example is shown in figure 2.3). The peaks in the spectrum correspond to the energy that is emitted by a specific electron transition of a specific element. For example, in figure 2.3 the two leftmost peaks correspond to energy emitted by an L-alpha transition and L-beta transition in the element lead.

The spectra can be processed using the software package AXIL [44]. This software can subtract background signals and determine net peak areas for all identified elements. This is done by fitting a mathematical model to the recorded energy spectrum.

The software package can also calculate meaningful chemical concentrations from the peak intensities [16]. This computation is based on the link between fluorescence intensity of a chemical element and its concentration. Effectively, this means that based on the recorded energy emitted by a K-alpha transition of lead for example, the concentration of lead at the targeted location is computed.
Chapter 2: X-Ray Fluorescence Spectroscopy

Figure 2.3: Example of a possible energy spectrum at the targeted location. Since each transition of each element has its own characteristic voltage, the elements can be identified by examining the peaks.

In theory, X-Ray Fluorescence Spectroscopy can be used to determine the concentration of most elements of the periodic system [29]. However, many element with a low atomic number (i.e. low Z-value) are difficult to measure and require advanced instrumentation, such that practical work is often limited to elements with an atomic numbers above 13. In addition, L-lines rather than K-lines are measured at higher atomic numbers (above 50) due to higher costs of equipment and difficult radiation protection measures.

Figure 2.4 shows the X-Ray fluorescence of the elements of the periodic system, given that only elements with \( Z > 13 \) are measured and that for elements with \( Z > 50 \) only the L-transition is recorded. It appears that in general the energy increases with the atomic number. However, due to the fact that for high-Z elements only the L-transition is measured, the emitted energy may be lower than for certain low-Z elements.

Using spectrum evaluation software, the exact chemical composition of a targeted point can be determined. The software can compute the concentration of all elements that correspond to certain peaks in the spectrum. As a result, each targeted point (pixel of the painting) can be represented as a vector of values, corresponding to the concentrations of the recorded chemical elements.

It should be noted that the recorded chemical elements can be present at any layer of the painting, i.e. at any 'depth'. This means that the chemical vectors are not very useful as a source of information about the hidden painting: sometimes the vector contains chemical values of the surface painting, sometimes of the hidden paintings and in most cases of both paintings.

2.2 Producing an elemental distribution map

By directing the beam along a whole area of a painting, the concentration of a particular element along this area can be obtained. At each point of the area the concentration of the element in question is computed from the net peak intensity of a recorded electron transition. For example, at each point of an area, the concentration of lead is computed from the recorded energy corresponding to an L-alpha transition.

The concentrations can be visualized in an image by relating the concentration with a colour: for example, a white colour corresponds to a high intensity whereas black corresponds to low intensities. Such an elemental distribution map is also called XRF map or XRF image.
Figure 2.4: Overview of the X-ray fluorescence energy of the elements of the periodic system. The red coloured dots show the electron transitions to the K-line and the blue dots the transitions to the L-line. Some dots are greyed out since they aren’t commonly recorded: the energy of low-Z elements is too low and for the high-Z elements, only the L-line transitions are measured.

Figure 2.5 presents four XRF maps (XRFs) acquired for the painting *Patch of Grass* by Van Gogh; the maps show the elemental distribution along the region indicated by the square in image A. The XRF maps of mercury, antimony, lead and zinc are shown by image B to E. The chemical concentrations are computed from L-transitions in case of mercury and lead. The concentrations of antimony and zinc are computed from the intensity of their K-transitions.

Several things can be deduced from the XRF maps. For example, the XRF image of mercury indicates that the lips of the woman contain relatively high concentrations of mercury. In addition, lead and zinc are either not used in the hidden painting or their energy doesn’t reach through the surface layer: the XRFs of lead and zinc don’t show much of the woman’s head.

As said in section 2.1, XRF analysis does not distinguish between layers: the energy recorded at a certain point can come from any paint layer. This means that the values shown by an XRF map also can correspond to any paint layer. For example, the high values of mercury visible at the top left corner of the mercury XRF probably correspond to the surface painting while the high values in the lower middle quite clearly correspond to the woman’s lips.

Some XRF maps are more likely to show the buried layer than others however. This is caused by their difference in energy emission strength. Each element emits energy of a specific voltage and when the voltage is very low, it is not likely that it can reach through a paint layer. Hence, it is not likely that the energy comes from an element in a lower layer since it wouldn’t be able to penetrate through the upper layers. The effect is that the XRF of an element that emits low-voltage energy probably doesn’t show a buried layer. High-voltage energy on the other hand can reach through all layers which means that the XRF map of such elements can show the hidden painting.
2.3 XRF applications in literature

As said in section 2.1, X-Ray Fluorescence Spectroscopy is now frequently used to analyse paintings. This section presents literature in which XRF is used to examine surface paintings. The chemical information helps to identify the pigments in the paint since the compounds are part of those pigments (see appendix B). The pigment information is often valuable for both art and conservation experts [29].

Two types of applications are addressed: using point measurements (section 2.3.1) and using XRF maps (section 2.3.2).

2.3.1 Analyses using XRF point measurements

The pigments of a painting are often analysed by using point measurements: X-Ray Fluorescence Spectroscopy is only performed on pre-selected points of the object. By examining the energy spectrum, the chemical composition of the paint at those locations can be estimated. If the points are selected with care (e.g. such that they represent distinct colours of the object), the conclusions can be very informative for the conservation expert.

Hochleitner et al. [17] examined not the paint of a painting but single pigment samples. They investigated approximately 500 different inorganic pigments, ranging from different types of white to yellow, orange, red, brown, blue, green and black. Their aim was to point out differences in the elemental composition of different pigments.

As an example, they showed the analyses of a number of blue pigments: Ultramarine, Bremer Blue and Cobalt Blue. For each pigment, they analysed samples obtained from different manufacturers and it appeared that it is not always certain that pigments with the same name...
also contain the same compounds. This is shown by the spectra in figure 2.6 where different samples of Ultramarine seem to contain different elements (e.g. pigment 94 doesn’t contain calcium while the others do).

**Figure 2.6: XRF spectra of different samples of the pigment Ultramarine (Hochleitner et al. [17]).**

**Ferrero et al.** [11] present a selection of case studies that illustrate the application of XRF to the pigment analysis of art objects of the Spanish cultural heritage. They used a portable device to analyse the elemental composition of various objects.

One case study shows the analysis of a painting by Joaquín Sorolla that obtained objective information about the materials he used. One of the conclusions was that Sorolla used Lead White in mixtures with other pigments in order to achieve different colours because lead was detected in all of the analysed pigments.

**Zieske** [53] studied nine watercolours by Cézanne to investigate Cézanne’s colour palette. She conducted elemental analysis of the major pigments by using XRF on a number of pre-selected locations. She was especially interested in the green colour because it was applied frequently but seemed deteriorated.

The presence of copper and arsenic detected by XRF indicated that that many strokes of dark green that occurred were indeed patches of previously bright emerald green watercolour that had deteriorated and darkened.

**Szökefalvi-Nagy et al.** [40] show how XRF can be used to determine whether a painting is a forgery or an authentic one. In some cases this is possible because the detection of a particular element can be evidence of a forgery. For example, when a certain pigment is not used at the time the painting is said to be painted.

Szökefalvi-Nagy et al. studied the example of identifying the presence of titanium at white coloured spots. Taking into account that Titanium White is available since about 1920, its presence provides an indisputable indication for either forging or later repainting. Indeed, the investigation of two paintings of Mészöly proved that they were forgeries, as was expected based on a rather strong consensus among the restorers that they were fakes.

**Hall and Tinklenberg** [14] used XRF to determine the relative concentrations of titanium (Ti), zinc (Zn), and lead (Pb) in lead-based house paints of different manufacturers. The objective was to demonstrate that these elements can be used to identify the manufacturer. It can
also provide a better understanding of past manufacturing practices and assist conservation.

They analysed multiple samples of each manufacturer. Figure 2.7 shows a three-dimensional plot of the relative concentrations of Ti, Zn, and Pb in the white house paints (for presentation clarity, only 30 paints are plotted). The data shows clear separations into clusters of the different manufacturers’ brands of paints. This means that when an unknown white paint sample is analysed, the resulting XRF spectrum can be used to determine the manufacturer.

![Figure 2.7: Three-dimensional plot of relative concentrations of Ti, Zn, and Pb in multiple samples of white lead-based house paints of different manufacturers, each having a different symbol (Hall and Tinklenberg [14]).](image)

Rosi et al. [35] examined two paintings by Paul Cézanne with XRF and infrared spectroscopy. Their aim was to characterize the elements used by Cézanne and try to put in evidence possible differences in the artist palette at the beginning and at the end of his career.

They selected a number of areas on the paintings for which they obtained the XRF spectra. The data for the green areas were the most complex to interpret because Cézanne employed both pure pigments and mixtures, obtaining a large variety of green shades. In order to better characterize the different pigments, Principal Component Analysis (PCA) was applied on the XRF spectra recorded only in the green areas.

Figure 2.8 shows the score on the PCA components of the green samples of the two paintings. The presence of three clusters in figure 2.8(b) provides evidence that the green shades showed different elemental compositions. In addition, since the clusters are composed of spectra collected from both paintings, Cézanne seems to have used similar pigments for both paintings.

2.3.2 Analyses using XRF maps

Instead of analysing specific points, XRF maps of a painting can be examined. These images, also called elemental distribution maps, show the concentration of a single chemical element for an entire region of the studied object (see section 2.2).

Chapter 3 addresses how XRF maps can be used to investigate hidden paintings. Here, studies are presented that use XRF images to examine surface paintings.

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1They actually used Fourier transform infrared (FTIR) spectroscopy, a measurement technique that collects the same infrared spectra but in a more sophisticated (and cheaper) way.
Figure 2.8: Score plots for the PCA components of the 17 XRF spectra recorded for the green colours of La Route Tournante (CZ1902) and L'étang des Soeurs (CZ1875) by Paul Cézanne (Rosi et al. [35])
Scott [38] presented a number of applications for XRF maps. One example is the investigation of a small oil painting on a copper support. The elemental maps illustrate the presence of different pigment areas (see figure 2.9). In addition, it seemed that the palette the girl in the painting is holding originally had a slightly different position. The shift is indicated with the arrows in figure 2.9 and it is good evidence for an original pentimenti.\(^2\)

![Figure 2.9: The painting An Allegory of Painting (on copper support) by Frans van Mieris, showing the results of elemental scanning for the indicated elements (Scott [38])](image)

A more elaborate study is given by Mantler and Schreiner [29]. They present examples of analyses by XRF of pigments in paint layers and illuminated manuscripts, iridescent glasses and medieval coins.

In one case study they examine a paint layer cross-section by means of XRF to illustrate the effect of shielding fluorescent radiation of one paint layer by other paint layers. For example, the paint comprised Vermilion mixed with Lead White and Red Lead mixed with Lead White but it was impossible to distinguish between the lead in different layers. The total intensities were also decreased with increasing thickness of the top layer.

Cotte et al. [7] present the analysis of materials in two paintings by Mathias Grünewald, an important painter of the German Renaissance. Preliminary analyses had revealed the presence of antimony, lead, and possibly sulfur. Antimony is usually associated with Naples Yellow (lead antimony) but this didn’t correspond with the colour of the pigment and the date of the painting. The main aim of the new study was therefore to determine whether the antimony are associated with lead and/or sulfur.

The analyses were conducted on three samples taken in regions where antimony had been identified. The XRF maps of the elements in the sample were examined to detect correlation: this would indicate that certain elements were chemically associated. In this case it appeared that antimony and lead were not correlated, whereas antimony and sulfur seemed to be linked (see figure 2.10). This led to the conclusion that the antimony was present as the pigment Stibnite (antimony sulfide) and not as Naples Yellow.

\(^2\)A pentimento (plural pentimenti) is an alteration in a painting, showing that the artist has changed his mind as to the composition during the process of painting. Marks revealing a totally different subject are not usually described as pentimenti.
As in the study of Ziekse, Cotte et al. [6] also use XRF in the context of degradation. The degradation is an important process to examine because a degraded pigment may have changed in chemical composition which requires a different treatment.

Cotte et al. have examined the blackening of Pompeian Cinnabar paintings (the pigment Cinnabar is also known as Vermilion). They collected four samples from a Cinnabar wall painting that corresponded to different degradation states and retrieved elemental distribution maps for each sample. By studying the XRF images for correlation between certain chemical elements and darkened colours, they were able to get insight into the degradation process of Cinnabar.

Figure 2.10: The XRF maps of antimony (Sb), lead (Pb) and sulfur (S) for two samples. There is no correlation visible between Sb and Pb, but Sb and S seem to be linked.
3 State of research on virtual reconstruction of hidden paintings

This section presents a review of existing literature on the topic of virtual reconstruction of hidden paintings, using XRF images. The studies are found with the search methodology described in appendix A.

Dik et al. [10] studied a painting of Van Gogh that contains a hidden layer with X-Ray fluorescence spectroscopy. Earlier examinations (including X-Radiography and Infrared Reflectography) of the painting Patch of Grass had already shown that there was possibly a woman’s head hidden beneath the surface though no facial characteristics could be recognised, see figure 3.1.

![Figure 3.1: Image A shows the painting Patch of Grass by Vincent van Gogh (Paris, April-June 1887). The red frame indicates the region shown in images B and C - rotated 90° counter-clockwise. These images are produced by X-Radiography and Infrared Reflectography respectively.](image)

They obtained XRF maps (XRFs) using synchrotron based radiation and a high-resolution detector. From these XRFs it appeared that mercury (Hg) and antimony (Sb) were the most noticeable elements of the hidden layer. This can be seen in figure 1.1 of section 1.1.

Based on the XRF maps and knowledge on painting pigments, a colour visualization of the woman’s head was constructed with Photoshop. At locations where Hg was measured, the pixels were given a red colour since they associated mercury with the red pigment Vermillion. Pixels located at areas with high intensities for Sb, were given a yellowish white colour because they found that antimony was present as the pigment Naples Yellow. The result of this ‘reconstruction’ is given in figure 3.2.

The main objective of the research of Dik et al. was to show that visualizing the concentration of certain chemical elements for a certain region of the painting can image the hidden painting more clearly than X-Radiography or Infrared Reflectography. By assigning colours to chemical elements with Photoshop they showed how their research could be used obtain a colour reconstruction of the woman’s head but they did not investigate reconstruction techniques.

Janssens et al. [23] also present an overview of the use of synchrotron XRF. A number of case studies are discussed, one of which is the visualization of invisible handwriting on a historic
Chapter 3: State of research on virtual reconstruction of hidden paintings

Figure 3.2: Colour visualization of the painting hidden beneath Patch of Grass made by Dik et al. [10] using Photoshop. It is constructed by assigning a red colour to high mercury intensities and a yellowish white colour to high antimony concentrations.

document. The document, a sales contract for an estate, showed signs of alterations (the original name of the owner had been removed by scraping) but the original text was unreadable.

The XRFs helped to obtain the original text: in the XRF map of calcium the (falsified) visible text could be seen while in the XRF map of zinc of the same area, a different text became visible. Apparently, the forger used different ink for the alteration, resulting in another chemical composition. Since the text was readable, Janssens et al. did not attempt to reconstruct the original text any further (e.g. retrieving the original colours).

Another approach used to examine hidden paintings is confocal XRF, a method that obtains elemental distribution maps including a ‘depth dimension’. This means that for each pixel it also is known at which depth, i.e. at which layer of paint, they are detected.

The method is investigated by Woll et al. [49] [50], Mantouvalou et al. [30] and Janssens et al. [22]. The main aspects are described below.

A confocal x-ray fluorescence microscope (CXRF) uses two optics placed perpendicularly to each other, such that depth information (i.e. layer information) can be acquired by gathering fluorescence only from the region of the sample where the two optics intersect.

The depth information can be very valuable for the examination of hidden paintings. XRF images may give an impression of a buried layer but the image remains a mixture of all layers. The CXRF technique can resolve this issue since it gives the ‘depth’ of a chemical element: the depth reveals at which paint layer the element is present. Now it can be determined which chemical elements belong to the surface painting and which to the hidden one.

Although the CXRF technique is very promising, it is not yet generally applicable. For example, given the time it takes to scan a sample\(^1\), only a small number of samples can be measured. This means that for most of an XRF image the depth information is not available. In addition, due to the high costs and practical issues, not many paintings can be examined with the CXRF microscope whereas the application of portable XRF\(^2\) is now amongst the standard techniques for characterization of elements in painted works of art [35].

\(^1\)To examine the painting The Armigers Shop, two separate experimental runs of approximately three days each were performed [48]

\(^2\)Currently, the portable XRF device produces lower quality images than the synchrotron facility but given the active research in this area, the results are expected to improve in the future.
There are two researches that examined XRF images to retrieve the hidden layer of the *Archimedes palimpsest* (a medieval parchment manuscript of Archimedes that has been overwritten with a religious text, see figure 3.3).

![Figure 3.3: A leaf (nr. 28 verso) of the Archimedes palimpsest. The arrows on the right indicate where the Archimedes text hidden underneath the top layer can be seen. (image retrieved from www.archimedespalimpsest.org)](image)

**Knox** [26] examined images taken of the palimpsest at different spectral bands (visible light and infrared) and XRF images. They characterized the different classes present at the parchment (Archimedes text, overwritten text and mould) with different spectral signatures. These signatures are representative vectors of values for the different bands. By visualizing how much each pixel resembles one of the signatures, it becomes clear to which class the pixel belongs.

Although retrieving the hidden text in the Archimedes palimpsest seems very similar to that of retrieving a hidden painting, there are a few important differences. The first difference is that the ink of the hidden text in the palimpsest pages is consistent over the entire page: the whole layer can be characterized using a single spectral signature. This will not be the case for a hidden painting since different parts of the painting consist of different paints.

Moreover, the spectral signature of the hidden ink is clearly different from that of the surface text. In contrast, the chemical elements used in the surface painting and the hidden painting can be similar. This means that if there would be spectral signatures corresponding to the surface painting and the hidden one, they might be very similar.

**Bergman and Knox** [2] try to visualize the hidden text by using a linear show-through model to separate different layers of text in the XRF images. In general, the show-through problem refers to the situation in which pages with double-sided printing are scanned and the printing on the back-side shows through in the scan of the front-side [39].

The show-through model uses the fact that a text is brighter in the image corresponding to the detector to which it is closer. In case of the Archimedes palimpsest, the hidden text is expected to be dark in one XRF image and bright in the XRF image of the reverse side.

The results of Bergman and Knox are promising but this approach is not directly applicable to the XRF images of a painting since there are in general no XRF images of both sides of the object. In addition, two XRF images of the same side of the object (corresponding to two different elements) cannot be used instead because they are not as correlated as two images from separate sides.
4 Object matching and inpainting: obtaining XRF of hidden painting

This chapter addresses the first subgoal of the research: the method that obtains XRF images of only the hidden layer of a painting. Such a step is necessary because the original XRF images are mixtures of all layers contained in the painting. Using these ‘mixed’ XRFs in the colourization process would result in a mixture of paintings and not in a reconstruction of the hidden painting.

First, section 4.1 explains the chosen methodology. The three separate steps of the procedure are addressed in section 4.2, 4.3 and 4.4 respectively. A discussion of the results follows in section 4.5, as well as a short conclusion.

4.1 Introduction: chosen methodology

This section discusses the methodology used to obtain XRF images that correspond only to the hidden painting. First, section 4.1.1 presents a short discussion of literature on separating image mixtures since an XRF could be seen as a mixture. Another approach, where regions in the XRF that belong to the surface painting are identified, is discussed in section 4.1.2. Finally, an overview of the chosen methodology is given in section 4.1.3.

4.1.1 Literature on separating image mixtures

The objective is to obtain the XRF of only the hidden painting. A direct approach would be to denote an XRF image as an image mixture such that the problem is similar to source separation: extracting the underlying sources of a mixture of two or more signals [52]. This process is called blind source separation (BSS) when it is done without strong additional information about the individual sources or constraints on the mixing process.

In general, BSS considers problems where a number of samples is given, each a (different) mixture of the same signal sources [25] (see figure 4.1). In most BSS approaches, these sources are estimated by maximizing the statistical independence of the original source signals.

Figure 4.1: Illustration of (blind) source separation techniques. They estimate the original sources of the signal mixture samples that are supplied.
BSS algorithms cannot be applied directly to XRF images. One reason is that the XRFs strictly speaking cannot be seen as samples of the same signal mixture: the sources mixed in one XRF may be different from those mixed in another XRF. Each XRF seems to be a sample of the same signal mixture, namely a mixture of the surface painting signal and hidden painting signal. However, the surface painting source in one XRF might be very different from the surface painting source in another XRF. For example, the ‘grass’ expressed in zinc is not the same image as the ‘grass’ expressed in mercury.

Furthermore, when an XRF is considered as a mixture of surface painting signal and hidden layer signal, the mixture is probably not linear: for example, the observed concentration of lead is not only the result of the lead in the hidden and in the surface layer but also of the presence of other elements, the thickness of the layers etc. This non-linearity makes source separation more complex: solving the non-linear BSS problem is in general not easy and requires additional prior information [25].

Other approaches that retrieve one of the images of an image mixture directly can be found in literature on retrieving text or images that have been overwritten. Chapter 3 addressed two studies that investigated how to retrieve the original text of the Archimedes palimpsest, a medieval parchment manuscript of Archimedes that has been overwritten with a religious text.

It was shown that these approaches were not applicable to retrieve hidden layers in XRF images. One reason was that the hidden layer of the palimpsest contained only one type of ink whereas a hidden painting consists of multiple regions with different paints. In addition, the presented show-through model cannot be applied since there are no XRF images of both sides of the object.

*Bleed-through* is a problem similar to that of show-through and occurs often in the field of cultural heritage. It refers to cases where the ink from the reverse side of an ancient document has seeped through, making the original text or image difficult to retrieve [43].

Tan et al. [41] point out that bleed-through requires a different approach than show-through. In case of bleed-through, the images on both sides may not be completely matched as in the show-through situation. However, the methods developed for bleed-through are very similar to those for show-through and require images of both sides of the object as well. For this reason these methods are also not applicable in the current research.

### 4.1.2 Indirect approach: identifying regions in XRF

As opposed to the direct approach, the XRFs of only the hidden painting could be obtained indirectly. In this case, the pixels of each XRF are first divided into two groups: those that concern the surface layer and those that concern the hidden painting. Then, the XRF of the hidden painting could be reconstructed using the hidden layer’s pixels and some inpainting technique [32].

Most XRF regions that belong to the surface painting are areas where the recorded energy comes from the surface painting (situation A in figure 4.2). However, there are also regions where the surface painting has blocked the energy from the hidden layer, leaving a dark area (situation B in figure 4.2). In both cases the area in question does not say anything about the use of the chemical element in the hidden layer, and as such should not be used in the reconstruction.

A method often applied to separate two layers in an image is *thresholding* [27]. In that case, the layers of the image are separated based on the pixel values: pixels with a value higher than the threshold correspond to one layer and pixels with lower values belong to another.
Thresholding cannot be applied in this way to find the pixels of the surface layer in an XRF image, since a pixel’s value doesn’t say anything about the layer in which the element is present (see section 2.1). This means that separating based on pixel value will not yield a surface and hidden layer.

An XRF image is actually a mixture of the XRF of the surface painting and the XRF of the hidden painting. Hence, to obtain only those regions that correspond to the hidden one, the XRF of the surface painting should be subtracted from the mixed XRF. An XRF of only the surface painting is unavailable but an ‘artiﬁcial XRF’ of the surface painting could be made based on its colours.

When the pigments of the colours are known (or can be estimated), the corresponding chemical elements can be determined as well. The translation from colours to pigments, and from pigments to chemical elements, is diﬃcult however. Moreover, this method would not give the regions of an XRF where the surface layer has blocked the energy from the hidden layer.

Another approach is to use the link between uniformity in colour and uniformity in a chemical element. When some pixels have the same colour, they are likely to have similar chemical elements as well. This indicates that an XRF can show similarities with the surface painting: wherever a certain pigment is used uniformly, the feature may show up on an XRF.

This approach is explicitly employed by a human observer. The observer would look at both the XRF and the surface painting and detect a hidden layer by tracing back features of the XRF to the surface painting (see figure 4.2). Subsequently, areas that cannot be traced back to the surface painting are said to correspond to some hidden layer.

To find the ‘surface painting regions’ in an XRF, digital image processing techniques could be applied, after which certain characteristics of the images can be compared. For example, edge detection [12] could be used to identify edges in both the surface painting and the XRF images and these edges could then be compared to find the ones of the hidden painting.

The drawback of edge detection is that the methods are often sensitive to noise, which is a problem in case of XRFs. In addition, finding hidden edges does not suﬃce since regions of the XRF that belong to the hidden painting need to be obtained.
Another approach using image processing techniques is texture-based comparison [12]. In case of the *Patch of Grass*, the surface painting has a significantly different texture than the hidden painting and separating based on texture is a possibility.

However, in other cases where the hidden painting is more similar to the surface layer, the texture is likely to be more similar as well. This would make the detection more difficult. Furthermore, the performance of this approach may also be reduced by the noisy character of the XRF images.

### 4.1.3 Overview of chosen methodology

Since there seem to be no suitable methods in literature that can retrieve (one of) the sources of an XRF mixture directly, the *indirect method* is chosen: first separating the XRF into regions that correspond to the surface painting and regions that show a hidden layer, then use the hidden parts to reconstruct the entire XRF of the hidden painting.

The chosen indirect approach follows from the point of view of a *human observer*. As said before, the observer looks for features in the XRF that are also found in the surface painting. More specifically, the examination of the observer mostly consists of *finding similar objects*: for example, a round shape in the XRF is said to belong to the surface painting if the surface painting shows a round shape at the same location. Objects that cannot be traced back to the surface painting are said to correspond to the hidden layer.

Finding objects of the XRF in the surface painting is possible since there is a relation between uniformity in colour and uniformity in a chemical element. If an area is painted in a certain colour, this whole area is likely to be painted with the same paint, with the same pigment(s). This causes all pixels of the area to contain the same chemical elements, in similar concentrations. Hence, the same area can appear on one or more XRF(s).

The steps of the separating procedure in this study are based on this ‘human approach’. To determine which parts of an XRF correspond to the surface painting, objects in both the surface painting and the XRF images need to be detected; this is discussed in section 4.2.

The second step is to compare the XRF-objects to the objects discerned in the surface painting to determine which XRF-objects belong to the surface painting and not to the hidden one. This step is addressed in section 4.3.

When the XRF is divided into two parts, the ‘surface-parts’ should be discarded before the XRF is used in the colourization process. This will leave holes in the image and section 4.4 describes how an inpainting algorithm can fill in these areas.

### 4.2 Object detection in surface painting and XRF images

This section addresses the procedures that distinguish objects in the XRF images and in the surface painting. These objects can be compared to determine the areas in the XRF images that correspond to the surface painting instead of the hidden one. This approach resembles that of a human observer, who would also try to find similar shapes in the XRF and the surface painting to locate the hidden composition (see section 4.1).

Discerning objects in an image is often referred to as *image segmentation*, a technique that tries to find distinct regions in an image [12]. The goal is to obtain regions that are uniform and homogeneous with respect to some characteristic and adjacent regions of a segmentation should have significantly different values for that characteristic [15].

Hundreds of segmentation techniques are present in the literature since there is no single
method that is good for all images, nor are all methods equally good for a particular type of image [33]. This implies that, although there are some general approaches, each application requires its own segmentation method.

In this study, the main objective is reconstructing a hidden painting: individual steps such as the segmentation, can be improved in future research. Therefore, relatively simple methods are investigated and the proposed segmentation algorithm should be seen as a starting point.

Section 4.2.1 starts by discussing the detection procedure for objects in the XRF images. Then, detecting objects in the surface painting is described in section 4.2.2. The method is somewhat different since the objects in the surface painting need to be found based on another characteristic, namely colour.

### 4.2.1 Finding objects in XRF images

As explained in section 4.1 the goal is to distinguish objects in an XRF based on their uniformity in concentration. This means that for each XRF, areas having pixels with similar values are seen as objects. A **thresholding algorithm** is a well-known method that can find such areas [33].

Thresholding is a common approach to image segmentation [36]. The main idea is to separate the data by grouping all pixels with intensities greater than a certain threshold into one class and all other pixels into another class.

In this case, thresholding is applied in such a way that *multiple* levels are distinguished; each XRF image is divided into several *slices*. Each slice contains pixels that have a similar value for the chemical element represented by the XRF.

The multilevel approach is used since the goal is to distinguish objects by finding areas that have similar chemical concentrations. When only two levels are used, an object may comprise many different grey values which means that it need not be painted in a uniform colour. The latter is required since this ensures that the object can also be found on the surface painting.

The number of slices determines the uniformity of the chemical values within an object. When a large number of slices are made, each slice contains values within a small range. Hence, the chemical concentrations comprised in the slice are all very similar, making the objects very uniform. Vice versa, a low number of slices implies that the discerned objects can comprise many different chemical concentrations.

The ‘ideal’ number of slices thus depends on how uniform the chemical concentrations of the detected objects need to be. Since the XRF measurements are not very precise (they depend on a number of factors, for example the layer thickness), requiring a very high uniformity is incorrect. On the other hand, when less uniform concentrations are allowed (e.g. when using two-level thresholding), objects may be found that are not painted in the same colour and this is not the intent either.

Just as a starting point, the XRFs are currently divided into five slices. Experiments with the XRFs of *Patch of Grass* have shown that for this painting, using five slices yields the best final result. However, when more data becomes available, the number of slices should be re-examined.

Before the slices are made, the values of each XRF are scaled to the range [0,1]. This scaling seems unnecessary since the range of each XRF is already the same (zero to 256). However, the actual maximum value of each XRF is different due to their difference in fluorescence power. Every element emits energy with different strength so the maximum energy that could be
recorded varies between elements (see figure 2.4 in section 2.1). The data is therefore scaled such that the minimum value is mapped to zero and the maximum to one.

Now that for each XRF the data ranges from zero to one, the range of values shown by a certain slice can be obtained. They are computed such that all values are divided into the requested number of slices. Hence, when five slices are requested each slice will have pixels within a range of \((1/5 = ) 0.2\) values.

Figure 4.3 shows the slices of the XRFs of the Van Gogh painting *Patch of Grass*. The white pixels in each slice are the pixels that have a value within the indicated range. Thus, the first slice of each XRF shows pixels with a value of zero up to 0.2, the second slice shows pixels with a value higher than 0.2 up to 0.4 and so on.

The 'objects' detected by the multilevel thresholding algorithm (i.e. the object formed by the white pixels in each slice) need further processing because a slice as a whole may not be traced back to the surface painting. Each slice actually contains a number of smaller objects that have pixels within the same range.

To obtain the separate objects, the Matlab function `bwlabel` is applied to each slice. This function uses the general procedure of Haralick and Shapiro [15] and defines objects by looking for connected pixels. For example, pixels that are connected with each other within an 8-neighbourhood are said to belong to the same object.

Figure 4.4 shows the result when `bwlabel` is applied to the slices shown in figure 4.3. Here, each separate object is shown in a different colour. Some colours may be indistinguishable since a certain slice may have more than 800 objects and it is difficult to distinguish 800 different colours.
Figure 4.4: Objects are formed in each slice of figure 4.3 using Matlab’s function bwlabel (method of Haralick and Shapiro [15]). Each object is visualized in a different colour though some colours may be indistinguishable: a slice may have more than 800 objects and it is difficult to distinguish 800 different colours.

4.2.2 Finding objects of surface painting

For detecting objects in the surface painting, colour should be used. This is explained in section 4.1: an area might show up on an XRF image when it is painted in a uniform colour since it is then likely that the area comprises a chemical element in a uniform concentration. The latter is required for discerning the area as an object on the XRF.

The literature on colour image segmentation is not as extensive as that on greyscale image segmentation [5]. Many studies use grey level image segmentation approaches with different colour representations. In this case, the same approach as described in section 4.2.1 is applied but the thresholding-step is replaced by colour quantization.

Colour quantization aims at reducing the number of distinct colours in an image while preserving the same overall colour appearance as the original image [37]. The colour quantization effectively divides the image into slices, similar to the XRFs (see section 4.2.1). Each ‘slice’ holds the pixels that have a similar colour: how similar depends on the number of slices. When many slices are made, each slice contains pixels with a very similar colour values. Vice versa, using a low number of slices results in many different colour values within each slice.

Similar to the XRF case, the multilevel approach is used to ensure that the discerned objects comprise only a small range of values, in this case colours. The exact number of slices depends on how different the colours represented by a single slice may be. Also in this case, five slices are made as a starting point.

In this study, the Matlab function rgb2ind is used for the colour quantization. This method uses minimum variance quantization; it works by associating pixels into groups based on the variance between their pixel values. For example, a set of blue pixels might be grouped together because they have a small variance from the centre pixel of the group.

Since five slices should be made, the colours of the image of the surface painting are reduced.
Chapter 4: Object matching and inpainting: obtaining XRF of hidden painting

to a set of five. Figure 4.5 shows the slices that are obtained when rgb2ind is used for this step. In white the pixels are shown that have RGB values within the indicated range.

Figure 4.5: Example showing how the pixels of the surface painting are divided into five slices: each slice shows the pixels that have an RGB value within the indicated range (the actual colours are presented as well).

Similar to the XRF slices, the slices of the surface painting are ‘containers’ of objects: each slice shows the pixels that have similar colours but they often form not one, but a number of objects.

To obtain separate objects, the same procedure as for the XRFs is applied. The Matlab function bwlabel finds all objects by looking for connected pixels. Figure 4.6 shows the result.

Figure 4.6: Objects are formed in each slice of figure 4.5 using Matlab’s function bwlabel (method of Haralick and Shapiro [15]). Each object is visualized in a different colour though some colours may be indistinguishable: a slice may contain more than 800 objects and it is difficult to distinguish 800 different colours.

4.3 Determination of hidden parts in XRF images

This section addresses the comparison procedure that is used to compare the objects located in the XRF images to those found on the surface painting. The purpose is to determine which objects of the XRFs (denoted as x-objects) are also found on the surface painting. This is said to be the case if an x-object resembles an object of the surface painting (an s-object) more than a predefined amount.

The problem is similar to that of shape matching: given two shapes, measure the resemblance between them and decide whether the similarity is greater than a threshold [45]. To do this, a similarity measure is required along with a threshold and the objects need to be represented by some shape descriptor. The shape descriptor represents each shape or object by its characteristics such that the similarity between different shapes can be measured more easily.
Section 4.3.1 discusses the use of a feature vector as a shape descriptor. The similarity measure, as well as the thresholds are addressed in section 4.3.2. Finally, the result is presented in section 4.3.3.

4.3.1 Feature vector as shape descriptor

Often the shape descriptor is a feature vector that uniquely characterizes a shape with a set of values [28]. By using such a numerical representation, the similarity measure becomes a distance measure: two shapes are alike when the distance between their feature vectors is smaller than a predefined threshold [51].

Finding suitable features can be complex because for many applications they have to be invariant under translation, scaling and rotation (e.g. finding a certain real-life object in a movie frame). However, in this case the objects should have the same shape and size, and appear at the same location in the image. This means that these aspects (shape, size and location) need to be described by the features.

In this study, the features that describe objects in terms of shape, size and location are taken from the Matlab function `regionprops`. This function measures a set of properties for each labelled region (i.e. object) in an image. By choosing the right set of properties, the required aspects of the objects are described by the features. The chosen properties are the following (see also figure 4.7):

- **Area**: the number of pixels in the region
- **Centroid**: the centre of mass of the region in terms of a horizontal and vertical coordinate. This property represents the location of the object.
- **Major axis length**: the length (in pixels) of the major axis of the smallest ellipse containing the region
- **Minor axis length**: the length (in pixels) of the minor axis of the smallest ellipse containing the region
- **Orientation**: the angle (in degrees ranging from -90 to 90 degrees) between the x-axis and the major axis of the smallest ellipse containing the region

![Figure 4.7: The properties used in a feature vector to represent an object’s shape, size and location.](image-url)
When the feature vectors are calculated, the values are normalized. Each feature value is divided by the maximum value possible for that feature. For example, the maximum value for the 'Area' feature is the size of the whole image. Hence, the feature value for 'Area' of each object is divided by this number.

Now, all objects found in the XRFs and on the surface painting can be represented by a set of numbers, i.e., for each slice a numerical matrix is acquired where the rows correspond to the objects and the columns to their values for each feature. In addition, the values of each column range from zero to one.

4.3.2 Similarity measure and thresholds

As said before, when the shape descriptor is a vector of numbers, the similarity measure becomes a distance measure \([51]\): it measures the distance between two points in \(\mathbb{R}^p\) space, where \(p\) is the number of features. In this case, the Euclidean distance is used since it is a straightforward metric that is applied in many types of applications.

Although all properties were measured at once, the Centroid-property is treated separately from the other features. The reason is that when the location of the object is mixed with the other features, some objects may be defined as 'similar' even if they do not appear at the same location. For example, if a certain object has exactly the same size and shape as another object but their location is different, they might still be classified as similar. This should be prevented because the location of the object is very important in case of the XRF images: only if they appear at the same spot they are a true match.

It should be noted that the properties remain linked since the Centroid is affected by the shape and size of the object. For example, if one object has a slightly different shape than the other, its Centroid will also be at a slightly different location but the objects may still be perceived as similar.

To compare the Centroids separately from the shape and size, two thresholds need to be defined. The first one determines whether an \(x\)-object is 'very near' an \(s\)-object. This is the case when the distance between the Centroids of the \(x\)-object and \(x\)-object is smaller than the defined threshold. Then, the second threshold determines whether the shape and size of the objects matches as well: when the distance between the feature vectors of the \(x\)-object and \(s\)-object is smaller than the second threshold, they are said to be similar based on shape and size.

Setting good thresholds is often done by training on a large dataset but in this case, only XRF images of the Van Gogh painting Patch of Grass are available. Therefore, exact numbers for the best thresholds cannot be given at this point.

The thresholds of the current study are chosen such that they are optimal for the Patch of Grass-images. In this case, an \(x\)-object has to be within a 5-neighbourhood of an \(s\)-object to match. In addition, the distance between their feature vectors should be smaller than 5% of the maximum distance (where the maximum distance is \(\sqrt{k}\) for two feature vectors holding \(k\) features, each having range \([0,1]\)).

4.3.3 Matching result

When the comparison procedure determines that an \(x\)-object is similar to an \(s\)-object, the area of the XRF that is represented by the \(x\)-object is assumed to show the surface painting and not the hidden one. Hence, the pixels of \(x\)-objects that match an \(s\)-object should not be used to reconstruct the hidden painting.

Figure 4.8 shows the pixels of \(x\)-objects that matched with an \(s\)-object as white pixels.
Hence, the black pixels show the areas where the XRF is likely to correspond only to the hidden painting and these areas should be used in the further reconstruction of the hidden painting.

Figure 4.8: Example of finding the areas of the XRF image that correspond to the hidden painting. In white, the pixels are shown that were part of an object that matched with an object of the surface painting. Hence, those pixels should be discarded and the areas indicated in black should be used in further reconstruction of the hidden painting.

To assess the performance of the matching procedure, some ‘reference images’ are required. The performance cannot be measured based on the real XRFs and the hidden painting: it is unknown what the XRF of the hidden painting looks like so that there is no ground truth. An indication of the performance can be obtained by applying the procedure on ‘fake’ images where the outcome is known or can be estimated.

The reference images are the greyscale version of the surface painting image and an image of another Van Gogh painting, showing the head of a woman. From each of those images, the preferred outcome of the matching procedure can be determined. All of the pixels of the greyscale surface painting image should be detected as part of the surface layer. In contrast, none of the pixels of the image with the woman’s head should be seen as surface painting pixels.

Figure 4.9 shows the results when the matching procedure is applied to the reference images described above. The top row shows the references and the bottom row the matching outcomes.

The outcomes correspond to a great extent with the desired results. Most of the pixels of the greyscale surface painting are detected as surface painting pixels: 47298 pixels are set to white, which is 75.7% of all pixels. Ideally, this should be 100%. In the other reference image, the Head of a Woman, the matching procedure finds 1994 pixels to be part of the surface painting. This is 3.2% of all pixels, where 0% would be ideal. This means however that 96.8% of all pixels are correctly identified as ‘hidden’.

A third test image is the XRF of lead. This is a special case since most pixels correspond to the ground layer of Lead White (between surface and hidden layer). All pixels that deviate from the average grey colour (e.g. black or white objects) should to be found as surface painting
Figure 4.9: To assess the performance of the matching procedure the algorithm is applied on two ‘reference images’: these are shown in the top row. The matching outcome is shown at the bottom row.

Figure 4.10: To assess the performance of the matching procedure the algorithm is also applied on a third ‘reference image’: the XRF of lead. The preferred outcome (shown at the bottom right) is obtained by finding all pixels that deviate from the average grey value. The actual matching outcome is shown on the bottom left.
pixels. This 'preferred outcome' is shown by the image in the middle of the bottom row in figure 4.10: when the image showing all average values grey values is inverted, the pixels in white now correspond to all pixels that deviate from the average.

The actual outcome of the matching procedure for the XRF of lead is shown by the image at the bottom left of figure 4.10. Here, 60198 pixels have the same value as in the preferred outcome, this is 96.3% of all pixels.

4.4 Using inpainting to complete the XRF

This section shows how example-based inpainting can be used to fill in holes that appear when the surface painting areas in the XRF are discarded.

The surface painting areas cannot simply be set to zero since that would imply that the chemical element is not detected at those locations. This might be incorrect: there is just no information there, the element may still be present.

Section 4.4.1 describes the inpainting procedure of Criminisi et al. [8]. Inpainting methods were investigated in a preliminary study and the algorithm of Criminisi et al. was expected to produce the best result [32]. The results when inpainting is applied to the XRFs of Patch of Grass are given in section 4.4.2.

4.4.1 Inpainting method of Criminisi et al.

The method proposed by Criminisi et al. [8] is meant for removing large objects from digital images. The challenge is to fill in the hole that is left behind in a visually plausible way, a procedure that is often referred to as inpainting.

Criminisi et al. combined ideas from two classical approaches to inpainting. The first class of algorithms aims at joining isophotes; the level-lines that represent upper boundaries of regions of equal grey values. Since isophotes are usually associated with the structure in an image, this approach works well on object boundaries. Reconstructing textured areas is often a problem; they tend to get 'over-smoothed'.

Inpainting algorithms of the second type, exemplar-based methods, are derived from texture synthesis. They try to fill in a missing region by copying a suitable patch from the remaining image. This patch is in general found with a texture-based search; the algorithm tries to find a patch that is likely to resemble the texture of the area to be filled in. The problem with exemplar-based methods is that they often have difficulty reconstructing object boundaries.

According to Criminisi et al., edges can be reconstructed properly with an exemplar-based method if a special filling order is used. They propose a filling algorithm that gives a higher priority to those regions of the target area that lie on the continuation of image structures. Using this approach, they succeed in filling in the edges correctly, as is shown in figure 4.11.

4.4.2 Inpainting applied to XRFs of Patch of Grass

An implementation of the algorithm of Criminisi et al. [3] was adjusted to use the black-and-white image produced by the object comparison procedure (see section 4.3.3). In these images, the white pixels are those that are part of an XRF object that has been detected on the surface.

\[\text{The main parts of an image are seen as structure: the objects whose surface is homogeneous without having any details. The texture of an image is seen on the surface of the objects. They are the details which make the images more realistic.}\]
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Figure 4.11: The algorithm of Criminisi et al. [8] demonstrated for the Kanizsa triangle (a famous optical illusion). The white area in image A is inpainted as shown by in-between images B to F, resulting in image G. Strong edges are reconstructed inside the missing region first.

painting. For this reason they need to be inpainted: since the energy recorded at those pixels relates to the surface painting, there is no information at that point for the hidden painting (i.e. there is a hole at that location).

Figure 4.12 shows the result when the inpainting procedure is applied to the XRF images. Here, the top row shows the original XRFs while the bottom row shows the reconstructed ones. In the middle the mask images are given that are produced with the object detection and comparison process of section 4.2 and 4.3.

4.5 Discussion of results and conclusions

Sections 4.2 to 4.4 have presented a procedure that reconstructs XRF images of only a hidden layer, from XRF images of the complete painting. This section discusses the results, addresses difficulties and suggests approaches to possibly improve the results. A short conclusion is given as well.

First, section 4.5.1 addresses the performance of the procedure that finds surface painting objects in the XRF images. The separate steps of this procedure as well as inpainting are discussed in section 4.5.2. Finally, section 4.5.3 presents the conclusions concerning the addressed subgoal.

4.5.1 Performance of surface painting detection

The performance of the object detection procedure is difficult to quantify since there is no ground truth: it is strictly speaking unknown which parts of an XRF shows elemental concentrations of the hidden layer of the painting. For this reason, the procedure is applied on some 'reference images' of which a preferred outcome could be estimated.

The results indicate that the matching procedure is able to correctly identify most of the XRF pixels. When the outcomes of all three test images are equally important, the average performance is \((75.7 + 96.8 + 96.3)/3 = 89.6\%\). This means that on average, 87\% of all pixels in an XRF are classified correctly.

The test results are a good indication of the overall performance but they are not conclusive. Only three images were used and two of them were no XRF images. This affects the results since XRF images are expected to contain more noise for example, such that correct object
Figure 4.12: Example of the inpainting procedure when applied to the XRFs of Patch of Grass, using the masks obtained by the object detection and matching algorithm of section 4.2 and 4.3.
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detection and matching is more difficult.

Qualitative assessment by visual inspection can also give an indication of the performance. As said in section 4.1, human observers are often quite capable of detecting the hidden painting’s composition in an XRF image.

In this case, visual inspection suggests that the performance is different for each XRF. Most of the light stripes in the upper left corner of the XRF of mercury are correctly detected as surface painting areas. The same holds for the black regions in the cheek of the woman, in both the XRF of mercury and of antimony. On the other hand, some additional areas of the Zn-XRF should perhaps been detected as ‘surface painting’ because a human observer would say that all stripes in the XRF of zinc correspond to the stripes of grass in the surface painting. In addition, in the antimony XRF two large areas on the right are identified as surface painting regions while this may not be the case: the visual inspection does not indicate that there are surface painting objects at those locations in the XRF.

4.5.2 Discussion of procedure steps

Visual inspection shows the difficulties for the object detection step. For example, the XRF of zinc seems to contain a lot of separate brush strokes, similar to the stripes of grass in the surface painting. However, the object detection procedure does not retrieve the separate strokes but detects only a few big objects.

The problem seems to be that the stripes in the zinc XRF aren’t very distinctive in their grey values and they are often connected. This causes the algorithm to see them as a single object. Since such an object is not detected on the surface painting (where the stripes are more distinctive and thus seen as separate objects) the stripes of the XRF aren’t matched to those of the surface painting.

Another reason may be that the stripes of grass are painted such that the zinc is not present in a ‘uniform’ way. The procedure only works if a single-coloured object also contains a single concentration of a certain chemical element. If for example a certain stripe of grass has one colour but the pigment Zinc White is not applied in the same concentration along the stripe, the stripe will not show up as a whole on the XRF of Zinc. Certain parts will be lighter than others, causing the algorithm to perceive them as different objects.

Assuming that not all separate objects are obtained, the matching procedure can be adjusted to find the right matches between the x-objects and s-objects. The comparison procedure is now designed such that entire x-objects have to match with entire s-object. However, in literature there are also algorithms for partial shape matching [4].

Partial shape matching methods are designed to detect situations in which two objects are not similar but some of their parts are. In case of the XRF images it might be worthwhile to use such an algorithm since surface painting objects are sometimes not present as a whole on the XRF image but parts of it are.

Instead of only comparing the XRF-objects to those of the surface painting, the objects of one XRF may also be compared to those of another XRF. For example, the XRF of mercury and that of antimony show the same dark regions on the cheek of the woman: the energy of both elements is blocked at those locations by the paint at the surface layer.

However, the similarity between objects from different XRFs does not necessarily indicate that those objects correspond to the surface painting. The pupils of the woman’s eyes for example, appear as objects in more than one XRF but they do not belong to the surface layer. Even if at all XRFs the pupils are dark, this does not mean that the paint of the surface layer
blocked the energy of the hidden painting.

The accuracy of the *inpainting* depends on a number of factors. For example, the larger the missing area, the lower the reliability of the reconstructed content: when the algorithm has little (boundary) information, it is difficult to find a good patch that can fill in the void.

In addition, the new content of the holes depends on the remaining image. For example, a missing area is only filled in with an edge if that edge was apparent at the boundary of the hole. Hence, if a lot of pixels need to be inpainted, there is little (boundary) information that can be extended and the resulting image will be rather flat and without remarkable features.

On the other hand, a mask containing too few pixels may also produce inaccurate results. When the detection algorithm marks too few pixels as surface painting pixels, some of the unmarked pixels are incorrectly seen as hidden pixels. This means that when the inpainting algorithm uses a patch from the remaining image as content for a missing region, this patch may very well belong to the surface painting, causing the hole to be filled in with incorrect information.

It may be possible to inpaint one XRF using information provided by other XRFs as well. For example, when for a certain region the concentration of mercury is unknown, the amount of antimony at that location may be used to find a suitable replacement patch for mercury. This approach only holds however when the chemical elements relate to the same pigment: if two chemical elements are part of the same pigment, their relative concentrations will be approximately the same all over the painting. For instance, since Vermilion consists of mercury and sulphur, the intensities of mercury and sulphur will always be correlated.

On the other hand, when two elements are not part of the same pigment, their concentrations need not be correlated. Hence, when the intensity of one of the elements is unknown at some location, the concentration of the other element does not directly indicate the concentration of the first.

### 4.5.3 Conclusions

This chapter addressed the first subgoal of the study:

*Develop a method that can obtain XRF images of only the hidden layer of a painting.*

This goal has been achieved by using a procedure consisting of three steps:

1. Objects are detected in the XRFs and in the surface painting based on uniformity in grey value (in case of the XRFs) and in colour (in case of the surface painting).

2. The objects of the XRF are compared to those found in the surface painting: when an XRF-object is more similar to an object of the surface painting than a certain threshold, the pixels of XRF-object are said not to correspond to the hidden layer of the painting.

3. The pixels that do not correspond to the hidden layer should not be used in the reconstruction process. They are therefore discarded and the holes that are left are filled in using an inpainting procedure.

The results indicate that the presented method can be seen as a good starting point. Quantitative results obtained using test images showed that on average 87% of all pixels are correctly identified as either surface painting pixels or hidden painting pixels. Since the inpainting procedure is able to reconstruct the holes that are left when surface painting pixels are removed.
from the XRFs, the obtained XRF can be seen as the XRF of only the hidden painting.

Further investigation of the intermediate steps could lead to better result. Currently, standard Matlab functions are used wherever possible. It might be worthwhile to investigate whether these methods could be replaced by other, perhaps more sophisticated algorithms. For example, partial matching techniques could improve the object comparison results.

It might also be beneficial to study entirely different methodologies such as Blind Source Separation or texture-based comparison (see section 4.1.1). Though these methods were not found to be directly applicable, they may be adjusted to work in case of XRF images.

To simplify the separating procedure, two approaches seem interesting. First of all, the confocal XRF (CXRF) technique described in chapter 3 would be very valuable. CXRF yields depth information for the acquired chemical intensities which could be used to determine what chemical information corresponds to which layer.

Secondly, Bergmann and Knox [2] (see section 3) have shown that a show-through model can be applied to separate layers in an XRF image. This approach was not applicable in this study since there are no XRF images from both sides of a painting. It would be very interesting however to investigate whether it is possible to obtain such images and whether a show-through model can be applied in that case.
5 Colourization by classification based on example painting

This chapter addresses the second subgoal of the research: the method that constructs a colour image of a painting that is represented by a number of XRF images. If the XRF images that are used only show a hidden painting (such as the XRF images obtained in chapter 4), the resulting image will also be a reconstruction of only the hidden image.

The methodology applied to achieve the second subgoal is addressed in section 5.1. The two main steps of the procedure are discussed in section 5.2 and 5.3 respectively. Finally, section 5.4 presents a discussion of the procedure and its results as well as a short conclusion.

5.1 Introduction: chosen methodology

This section describes the approach that is used to obtain a colour image from XRF images. First, colourization algorithms found in literature are addressed in section 5.1.1. Section 5.1.2 discusses the approach where the chemical values are used to determine colour. An overview of the final methodology is given in section 5.1.3.

5.1.1 Example-based colourization

The goal at this stage is to obtain a colour image from XRF images. Since the XRFs are greyscale, the problem seems related to that of colourization: converting a greyscale image to a colour image. This topic was addressed in a preliminary research [32] and a short overview is given here.

The main difficulty of colourization is that a single grey value can map to different colour values since different colours may have the same grey value. This means that for any colourization, additional information is needed. Two general approaches are used in literature:

- **Example-based** methods search in an example image for pixels that resemble the pixel to be colourized, or for regions that are similar to regions that need to be colourized. The resemblance is based on some statistics of the pixel and its neighbourhood.

- **Scribble-based** methods require that a user applies some colour scribbles to the image. The rest of the image is colourized by propagating the samples to the other pixels, for example by minimizing colour differences in small neighbourhoods or by blending several samples based on the distance between pixel and samples.

Scribble-based colourization could work for XRF images but the user (e.g. conservation expert) may not know which colours to apply. In addition, the 'discontinuous' character of the image, due to both noise and painting technique (e.g. lots of separate brush strokes), can cause the propagation to fail.

Example-based colourization seems to be a good approach since there are often example images available: in many cases a painting can be found that contains colours that are likely to resemble those of the hidden painting.
Figure 5.1 illustrates the main approach of example-based colourization algorithms. The following steps are taken:

1. The example image is converted to greyscale (image B is converted to image C).

2. The source image (image A) is scanned: for each pixel some statistics are collected such as its grey value, the average grey value of its neighbourhood and the standard deviation in the neighbourhood.

3. For each greyscale pixel, the algorithm searches in the example image for the pixel with statistics that are most similar to those of the greyscale pixel (the algorithm looks in image C for a match with the selection in image A).

4. The colours that the best-matching example pixel has in the original example image are used to colourize the corresponding pixel in the source image (the colours of the matching selection are found in image B and used to produce image D).

![Figure 5.1: An illustration of example-based colourization. Image A is colourized using example image B: each pixel of image A is matched with a pixel of image C and the colour that the latter pixel has in image B is used to obtain the colour of the pixel in A. This results in image D.](image)

It should be noted that this is the most general approach of such algorithms. There are many different techniques using different steps. Some algorithms include for example a segmentation phase and search for matching pixels in particular regions.

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**Pixel values should be luminance values**

In general, if the actual colours of a greyscale source image are unknown, the image is said to be colourized correctly if a human observer thinks the colours are 'plausible': the clouds are white and the grass is green. This implies that the pixels of the greyscale clouds need to be matched with the pixels of the clouds in the example image, and the grey grass pixels with the coloured grass pixels.

For this to happen, the greyscale patterns of the clouds in the source image should be similar
to those of the clouds in the example. Hence, since the clouds in the example are lighter than their surroundings, the cloud pixels in the source image should also be lighter than the pixels of their surroundings.

More generally speaking, for ‘correct’ matches the greyscale patterns of the source image need to be similar to those of the example. The greyscale values in the example effectively represent the luminance of the pixels, i.e. how light or dark a pixel appears. Hence, for correct matches, the pixel values on the source image should also indicate the luminance of each pixel.

However, the grey values of an XRF need not be consistent with the actual luminance of the pixels. A pixel value of an XRF represents the intensity of a certain element, i.e. a light pixel indicates that a high concentration of that element is used there. This does not mean that the pixel at that location in the hidden painting actually has a light colour. For example, if dark red is painted with a pigment that contains a lot of mercury, the XRF of mercury will be very light at areas where the artists painted dark red.

It is therefore incorrect to use an XRF as input to the example-based colourization procedure. The following example illustrates the problem when example-based colourization is applied to an XRF:

Assume that an example-based colourization algorithm is applied directly to the XRF of mercury (Hg) of Patch of Grass (image A in figure 5.2), using the example given by image B of figure 5.2. The algorithm will examine each pixel and its neighbourhood of image A and look in image C for a pixel with the same characteristics. So, when studying pixels of the woman’s mouth, the algorithm searches in image C for pixels that are white themselves and have a fairly dark neighbourhood. However, the mouth of the woman depicted in the example doesn’t have these characteristics: here, the mouth is relatively dark compared to its surroundings. Therefore, the algorithm may not match the source pixels from the mouth to the example pixels of the mouth but to another part of the example image. Hence, the mouth in image A might receive colours that belong to something other than the mouth of the woman in image C.

![Image A is the XRF of mercury of Patch of Grass. Image B shows another painting by Van Gogh (called Head of a Woman, from winter 1884-85, Nuenen) that resembles the hidden painting. The greyscale version of the example is given by image C: this image would be used in example-based colourization algorithms to determine the colours of image A.](image)

5.1.2 Translating chemical values to colours

Colourization algorithms presented in literature cannot be applied since the values of the XRFs do not correspond to luminance values but to chemical intensities. The chemical elements do relate to colours however and this section investigates whether the colour can be deduced from chemical values.
The colours in a painting are the result of the use of pigments and these materials have distinctive chemical compositions (see appendix B). The pigment ‘Cadmium Yellow’ consists of cadmium-sulfide for example while ‘Egyptian Blue’ is a calcium copper silicate.

X-ray fluorescence analysis has been demonstrated to be of great value for the characterization of artists palette because it provides information about the chemical composition of the paint (see section 2.3). If the chemical composition of a pixel is given by the XRF, the pigment applied at that location may be determined.

... Link between a pixel's chemical composition and its colour

Given the above reasoning, it seems straightforward to convert a set of XRFs to a colour image: look at the chemical composition of each pixel, deduce the pigment and set the corresponding colour. However, the XRF technique has some important limitations, making it practically impossible to deduce the exact pigments from the recorded intensities [35].

The emission intensity of each element depends not only on its concentration but also on the overall composition of the area under investigation (e.g. layer thickness). In addition, the XRF only shows the single elements and an unambiguous identification of the corresponding pigment is not always possible. For example, the elements copper, lead, cobalt and chromium are each contained in a number of different pigments, with different colours.

The limitations are especially troublesome for the modern artists palette, because those can contain both natural and synthetic pigments, as well as complex mixtures (mixed by either the artist or used as ready-made tube paint).

Although the chemical composition of a pixel cannot be linked to the colour of a pixel directly, it seems reasonable to assume that if two pixels have different chemical values, their colour is also different. The rationale behind this assumption is that two different chemical compositions correspond to two (mixtures of) different pigments or similar pigments but with different concentrations. The latter would also cause a difference in colour: the colour of Naples Yellow becomes more reddish when more lead is used for instance.

Based on this assumption, objects of different colours can be distinguished in the XRF data, even though the actual colours are unknown. This is done by applying clustering, i.e. grouping pixels based on their chemical compositions. All pixels of such a ‘chemical cluster’ are assumed to be painted with the same (unknown) colour.

... Linking example colours to chemical clusters

Although different coloured objects could now be found, still it is unclear which colour the pixels have. As alternative source for the colour information an example image can be used that is submitted by an art expert. This expert is able to supply an image that contains colours that are likely to be used in the hidden painting.

To determine which example colour is used for which chemical cluster (without using chemical information), an idea presented by Greenfield and House [13] could be used. The objective of Greenfield and House was to recolour a source image based on the colours of an example using ‘palette matching’. They construct the palette (i.e. a set of representative colours) of both images and then make associations between those palettes.

The colour responsible for the largest area of the source image is matched with that of the example. Then, further pairing of colours is done by examining their relative deviation from these anchor colours.

In case of the XRF data, the ‘palette’ does not contain colours but chemical compositions. Although the distance between those compositions can be computed, matching these distances...
with distances between colours of the example fails.

Assuming that the distance between two chemical clusters is \( X \), they should be linked to two colours that also have a distance of \( X \). However, this might be the case for red and blue and for red and green: the distance between red and blue is similar to that between red and green. This example shows that matching based on relative distances does not yield unambiguous colour assignments.

### 5.1.3 Overview chosen methodology

Since chemical values do not correspond with luminance values, colourization algorithms found in literature cannot be applied. The chemical values relate to certain pigments but a direct translation is practically impossible.

Pixels can be grouped together based on their chemical values and these groups are likely to correspond with different colours. The actual colours are still unknown however and linking the colours of an example to the chemical clusters is not straightforward.

Instead of clustering, classification is required. A clustering procedure assigns chemical compositions to unknown classes but for the colourization they should be assigned to known classes, namely the colours of the example image. This is called supervised classification \[21\]: the chemical composition of a pixel needs to be recognized as a composition corresponding to a specific colour in the example image.

For this, some labelled patterns are required such that the recognition system learns which kind of patterns correspond to which class. Labelled patterns refer to points in the example image where the colour as well as the chemical composition is known.

In this study it is therefore assumed that the chemical composition of the colours in the example is known. This is a reasonable assumption since they can be obtained by XRF point measurements and such analyses (with portable XRF devices) are done frequently \[35\]. Otherwise, the chemical values of the example image need to be estimated.

The construction of the training set (i.e. set of labelled patterns) and the classifier itself are discussed in section 5.2. Section 5.3 describes how the trained classifier is applied to actual XRF data.

### 5.2 Classifier design and training using example image

This section discusses the classification approach used to determine the colours of the pixels represented by the XRF data. The classification uses training data supplied by an example image to learn which kind of chemical compositions correspond to which colours of the example.

Obtaining training data from an example image is addressed in section 5.2.1. Section 5.2.2 discusses which classifier is used to classify the chemical compositions given by the XRF data.

#### 5.2.1 Creating training set of example data

The training set consists of the feature vectors and class labels of the training samples: the feature vectors are the chemical compositions of the samples, the class labels are the colours at corresponding locations.

**Feature vectors**

The training samples can be supplied as the results of XRF point measurements that are
performed on the painting that serves as an example. These analyses give the chemical composition at certain locations of the painting such that at these locations, the colour as well as the chemical elements are known.

The number of required point measurements depends on the colours of the example image. For most images the colour information can be represented by a set of few quantized colours, typically ten to twenty [9]. This would imply that at least ten measurements are required. It is however preferred that there are multiple measurements for each colour since a larger training set will in general improve the classification results [34].

Although the complete chemical composition for an example pixel is given by a point measurement, there are often only a few XRF images that show the hidden painting’s composition, for example two or three. This means that for the pixels of the hidden painting, the chemical compositions consist of only a two or three intensity values. These compositions need to be classified so the classifier should also be trained on only the example’s values for these elements.

In case of the painting Patch of Grass, only the XRF images of mercury (Hg) and antimony (Sb) show the hidden painting. Hence, of all point measurements, only their values for Hg and Sb should be used in the training.

A training dataset could also be made without actual XRF point measurements by estimating the chemical values. The approach is then to express the colours of the example image in terms of the required chemical elements. For example, when mercury values are required and it is known that mercury is used as red in the painting, the ‘redness’ of a pixel can be taken as its value for mercury.

Such a translation is made for an image of a painting that resembles the painting hidden beneath Patch of Grass. This example is shown as image A in figure 5.3. Image B and C show the estimated amounts of mercury and antimony respectively: the ‘redness’ is used as estimate for mercury and the ‘lightness’ as the estimate for antimony (since antimony is here associated with the pigment Naples Yellow, a light colour).\footnote{The chemical estimates are computed by converting the example image to Lab colour space: the $a$-channel value indicates how red a pixel appears (which is the estimated concentration of mercury) and the $l$-channel value gives the luminance of a pixel (which is used as the estimated amount of antimony).}

![Figure 5.3: Image A shows a cut-out of the painting Head of a Woman by Van Gogh that resembles the painting hidden beneath Patch of Grass. The ‘redness’ of each pixel is used as estimate for the amount of mercury at that location (image B), the ‘lightness’ as estimate for the antimony concentration (image C).](image)

The data collected from the example is represented in a matrix or dataset. Here, the rows correspond to the observations, in this case the pixels. The columns represent the variables or features, in this case the chemical elements. Thus, each pixel is represented by a vector of
numbers, namely the values for the chemical elements of which there is an XRF image.

To ensure that the classification is independent of measurement units, the data must be scaled \[46\]. The values are scaled for each element separately in such a way that the feature values represent relative amounts: the minimum observed value for a single chemical element is mapped to zero and the maximum to one.

A pattern classification procedure usually contains some form of feature selection or extraction \[46\]. The main purpose of these techniques is dimension reduction: by reducing the number of features, redundant or irrelevant information is removed for example, which may improve the classification result.

In case of the XRF data however, the number of features is already low. The number of features depends on the number of XRF images that show the hidden painting since the values for these elements are used as features. Given that often only two or three XRF images show a buried layer, the number of features will be low as well.

\[
\text{\ldots Class labels}
\]

The class labels are the colours that are visible on the example image at the locations of the point measurements. It is therefore important to register these locations such that the colours can be retrieved from the example image.

When no point measurements are used but the chemical concentrations of the example image are estimated, the class labels are the colours of each pixel of the example image. However, there may be as many colours as there are pixels. Therefore, colour quantization should be applied and the retrieved colour indices are used as labels.

The colour quantization can be done as described in section 4.2.2, with Matlab’s \texttt{rgb2ind}. Since the colours of most natural images can be represented by a set of ten to twenty colours \[9\], the number of colours of the example is reduced to twenty.

This procedure should not only yield colour labels but also a colour map, where the colour values corresponding to the colour of each label are stored. This is shown in figure 5.4: the colour map on the right shows which class label correspond to which colour. After the new patterns have received their colour labels, the precise colour can be retrieved using the colour map.

![Figure 5.4: On the left, the example painting given by image A of figure 5.3 is shown after colour quantization is applied to reduce the colours to a set of twenty. A close-up is presented in the middle, showing a close-up of the woman’s mouth. The bar on the right is the colour map that shows which class labels correspond with which colours.](image)
5.2.2 Choosing a classifier

Once the example data is represented by a dataset, the classifier should be designed. Jain et al. [21] identify two main approaches to classification:

- The simplest and the most intuitive approach is based on the concept of similarity: patterns that are similar should be assigned to the same class. In this case patterns can be classified by template matching.

- In statistical classification, each pattern is represented in terms of \(d\) features and is viewed as a point in a \(d\)-dimensional space (the feature space). The objective is to find decision boundaries in this space that separate patterns belonging to different classes.

In this study, the template matching approach is studied for two reasons. First of all, the objective of this research is to present a starting point for the virtual reconstruction of hidden paintings. The classification is an intermediate step that can be improved in future research. For now, template matching is a good approach since it is a straightforward method that can still obtain good results [21]. Secondly, template matching also fits with the size of the training set. When the training set is made up of XRF point measurements, the number of samples will be low: only a limited number of point measurements are usually taken (ten to twenty). Such a small training set makes it difficult to obtain good results with a more complex classifier [34].

According to Jain et al. [21], the most straightforward one nearest-neighbour decision rule (1-NN) rule is a good a starting point since it appears to always provide a reasonable classification performance in most applications. With the nearest-neighbour approach, each pattern in the training set is a template. An unlabelled pattern is classified by assigning the label which is most frequent among the training samples nearest to that pattern. The distance is commonly measured using Euclidean distance.

The 1-NN approach is a good method to use in this study since it does not require any user-specified parameters (except for a distance metric). This means that the implementation is very straightforward. However, results may be improved by using more neighbours.

In general, the larger the number of neighbours \((k)\), the more robust the procedure will be [46]. This is caused by the fact that the effect of noise is reduced when more neighbours are taken into account. The value for \(k\) should however be small in respect to the number of training patterns, so that the neighbourhood is still the local neighbourhood of the sample.

The optimal choice for \(k\) can be found using cross-validation. Each pattern of the training set is then classified using the remaining samples for various values of \(k\) such that the overall performance can be computed. In this case, experiments showed that the optimal number of neighbours is mostly found to be five; three, seven or nine neighbours are found often as well. Therefore, when the classifier is applied to the actual XRF data, results of all four options are given.

A disadvantage of the nearest-neighbour approach is that the classification can be become computationally expensive for a large dataset since then many comparisons have to be made. However, if the point measurements are used as example data, the number of templates to which the chemical patterns need to be compared is limited since in most cases only ten to twenty measurements are taken.

When for each pixel in the example its chemical values are estimated, the training set will be large (e.g. 62500 patterns for an image of 250x250). In this case, the computation time can...
be reduced by using a random subset of the training dataset. This is also done in the current study: from each class 100 samples are randomly selected such that the training set contains 2000 samples in total (due to the colour quantization, there were 20 different colour classes defined for the example image).

5.3 Applying classifier on XRF data

This section discusses how the classifier as presented in section 5.2 can be applied to the actual XRF data, in this case the data from the painting *Patch of Grass*.

To apply the nearest-neighbour classifier described in section 5.2 to true XRF data, the data should be formatted similarly to the training set. This means that the input variables must first be scaled.

The same scaling as for the training set is applied: the values are scaled for each element separately in such a way that the minimum observed value for a single chemical element is mapped to zero and the maximum value to one. As described in section 5.2.1, no feature selection or extraction is applied.

The nearest-neighbour classifier used in this study is the *knnc* function of PRTools, a Matlab toolbox that supplies user routines for traditional statistical pattern recognition tasks [18]. The best number of neighbours can also be determined with this function as it can optimize the value of $k$ using cross-validation.

As said in section 5.2.2, experiments showed that for the estimated XRF data of the example image, the optimal number of neighbours was five. However, three, seven and nine neighbours were often found by the *knnc* function as well and therefore all four options are used here.

The *knnc* function is first applied on the training set, i.e. the dataset consisting of data and labels of the example image (see section 5.2.1). This yields a mapping: the classifier is trained to map a $k$-feature data vector to a 1-dimensional output space, i.e. the class label.

The trained mapping can then be applied to the actual XRF data such that each feature vector is assigned to a specific class, namely the class that appears most frequent among the templates that are most similar to the new pattern.

After the classification, the assigned class labels are used to obtain the colours of the pixels. When the colours are given by point measurements, the class label indicates with which point measurement the new XRF feature vector is matched. The colour at this point in the example image is applied to the pixel represented by the XRF feature vector.

In case the chemical values of the example image were estimated, the class labels correspond to the quantized colours of the example. These were stored in a colour map, such that for each label, the corresponding colour can be retrieved. Hence, the colour of each pixel can be looked up in the colour map using the label assigned to its XRF feature vector.

The top left image of figure 5.5 shows the result when a one nearest-neighbour classifier is used on the data given by the mercury and antimony XRF maps of *Patch of Grass*. The example shown at the top right of the figure is used, with the estimated values for mercury and antimony values as presented in figure 5.3. Only the chemical values for mercury and antimony are required since only those XRFs show the composition of the hidden layer.

Colourization results when using three, five, seven and nine neighbours are also shown in
Chapter 5: Colourization by classification based on example painting

5.4 Discussing of results and conclusions

This section discusses the method and results presented in section 5.2 and 5.3. There, it was described how classification applied to XRF data obtains a colour image when a training set is constructed from data of an example painting.

First, the performance of the classification is discussed in section 5.4.1. Section 5.4.2 addresses the training data (i.e. example image) that is used in the procedure, as well as the classifier. A short conclusion is given in section 5.4.3.

5.4.1 Classification performance

It is difficult to quantify the performance of the classifier since the true colours of the hidden painting are unknown. The labels (i.e. colours) that are assigned to the chemical compositions (i.e. pixels) cannot be checked against their actual labels.

It is possible to assess the performance qualitatively using visual inspection. A human observer could examine whether the pixels of the reconstruction have received a colour of the example that is expected at those locations.

In case of the Patch of Grass, the virtual reconstruction shown by the ‘$k = 5$’-image in figure 5.5 is examined. This is the result of applying a 5-nearest-neighbour classifier to the XRF data comprised of values for mercury and antimony. The classifier was trained on the estimated chemical values of the first example image, shown in figure 5.3.

The visual inspection suggests that the classification performs reasonably well. The woman’s head is clearly visible and the light and dark areas are consistent with the example: shadows and highlights are located in the same regions of the composition. Moreover, there is a red colour visible at the lips of the woman, which corresponds with the red lips of the woman in the example.

On the other hand, the colours of the obtained image appear rather uniform. This seems to be consistent with the example image, that doesn’t have many different colours as well. However, the main difference is that the colours in the example appear clustered, forming uniform regions of colours. In the XRF colour image, the colours are more ‘mixed’, causing an overall brown tint.

The mixing is caused by the classification: pixels in the same region are classified to different classes, causing them to get different colours. The result is that each region contains the same colours, albeit in different amounts (see figure 5.7). This makes the overall appearance uniform.

Visual inspection of the virtual reconstructions obtained with the second example (shown in figure 5.6) indicates a similar performance: shadows and highlights are located at the expected
Figure 5.5: Colourization results using different numbers of neighbours in the $k$-nearest-neighbour classification applied on the mercury and antimony XRF maps of Patch of Grass. The data shown in figure 5.3 is used to train the classifier; for convenience, the example image is repeated here in the upper right corner.
Chapter 5: Colourization by classification based on example painting

Figure 5.6: Colourization results using different numbers of neighbours in the $k$-nearest-neighbour classification applied on the mercury and antimony XRF maps of Patch of Grass. The example image used for the training data is shown in the upper right corner; its chemical values are estimated as described in figure 5.3.
regions and the lips are correctly colourized with more red. On the other hand, the colours of this reconstruction appear rather uniform as well, implying that the classification again assigns different colours to pixels of the same region.

![Figure 5.7](image)

*Figure 5.7: The close-ups of the virtual reconstruction (obtained with a 5-nearest-neighbour classifier) show that each region is actually a mixture of the same colours, instead of a uniform region of one colour.*

### 5.4.2 Training data and classifier

The colours that are used in the reconstructed hidden painting need not be assessed because they are taken from the example image that is supplied by an expert. Since this example is chosen such that its colour are likely to resemble those of the hidden painting, the colours of the virtual reconstruction are similarly consistent with those of the actual hidden painting. This means however that the example image should be chosen with great care.

To obtain a virtual reconstruction with the exact colours of the real hidden painting, the example image should contain exactly those colours that are used in the hidden composition. Since these colours are unknown, it may be difficult to find such an example but the chemical data does provide some clues. For example, the presence of certain chemical elements may be evidence for the use of certain pigments and hence, a certain colour. Combining the chemical information with knowledge on the artist’s usual palette, (estimated) date of the painting and its place of origin, an art expert may be able to select an example painting that is likely to contain the colours of the hidden painting.

The procedure may be extended to use multiple example images. The images can be used to obtain more training samples, which may increase the reliability of the classification. The examples may provide the same information or each example image is used to give information on a particular aspect. For instance, two different examples may provide chemical compositions of two different sets of pigments.

Another approach is to obtain a colourization for each example image separately and then combine the results. For example, the final colour of a pixel may be the colour that is most frequently assigned to the pixel or the average colour of all outcomes for the pixel. This could also improve the colourization result.

The virtual reconstructions shown in this study are based on estimated chemical values of
the example image. This was sufficient to illustrate the use of a classifier to obtain colours. It should be noted however that the quality of the colourization depends greatly on the exact translation.

The colours that are assigned to the XRF pixels depend on which chemical compositions are formulated for the colours in the example image. If these are incorrect, the colours that are assigned to the XRF values are incorrect as well.

To estimate the chemical values of the example painting correctly, again the knowledge of an expert is required. For example, when the colours need to be expressed in terms of cobalt, it is not immediately clear which kind of characteristic can be used to estimate the cobalt concentrations: either the amount of yellow or blue should be used as estimation for the cobalt, depending on whether the cobalt is associated with Cobalt Yellow or Cobalt Blue in this case.

In this study, the nearest-neighbour classification approach is applied to obtain a starting point. Experiments showed that the number of neighbours did not affect the colourization very much but the leave-one-out cross-validation showed that for this painting, \( k = 5 \) was often the optimal choice. The best \( k \) may be different for other paintings however so performing multiple experiments with different numbers of neighbours is recommended.

A different classifier could be used as well but it is unclear whether this would improve the results. For example, statistical classifiers make often assumptions about the underlying probability density functions of patterns in a class. It should be studied whether it is possible and reasonable to make correct assumptions.

5.4.3 Conclusions

This chapter addressed the second subgoal of the study:

\[ \text{Develop a method that can construct a colour image of a painting that is represented by a number of XRF images.} \]

This goal has been achieved by using a procedure consisting of two steps:

1. An example image is used to obtain a dataset that shows which chemical composition corresponds to which colour in the example. The data is subsequently used to train a nearest-neighbour classifier.

2. The classifier assigns each chemical compositions of the actual XRF data to a certain class: a specific colour of the example image. This way a colour image is obtained.

Visual inspection of the reconstructions made with a 5-nearest-neighbour classifier suggests that classification can indeed be used to obtain a colour image from XRF data. The pixels are in general classified correctly: the colours of the image regions correspond with what is expected based on the given example image. Moreover, the performance seems to be consistent since they were obtained using two different example paintings.

The performance is highly dependent on the supplied example image. This image should therefore be chosen with great care and such that its colours are likely to be similar to those applied in the hidden painting.

The performance also depends on whether the chemical values of the example colours are estimated or given by XRF point measurements. The latter is preferable as it improves the reliability of the colourization. Estimating the chemical values of colours is rather complex and the knowledge of an art expert is required for good estimates.
The experiments were inconclusive concerning the optimal number of neighbours used in the classifier. Cross-validation indicated most often that five neighbours should be used but three, seven and nine neighbours were also frequently found. When the classifier is applied on data of other paintings, further experiments are recommended.

Colourization results may be improved by using multiple examples. It could increase the size of the training set which in general leads to more reliable classification. Another option is to obtain a colourization for each example separately and combine the results.

It may also be possible that an entirely different classification approach improves the colourization result. This requires further investigations however because it is not immediately clear whether different classifiers are applicable and likely to produce better colourizations.
6 Conclusions

This chapter presents the conclusions of the thesis research. Section 6.1 shows how the main research objective has been achieved and section 6.2 presents a discussion of the results, with respect to future research.

6.1 Concerning the main research objective

The main objective of this study was:

*Develop a method that uses XRF images to produce a virtual colour reconstruction of a hidden painting in such a way that the reconstruction contains colours that, according to art experts, are consistent with the real hidden painting.*

This goal has been achieved by describing two procedures that, when combined together, can produce a virtual reconstruction of a hidden painting. The image contains the correct colours when an example painting is supplied that is expected to have similar colours as the hidden painting.

The following two procedures were presented:

1. *Chapter 4 has shown that XRF images of only the hidden layer of a painting can be obtained using object matching between the XRFs and the image of the surface painting, combined with inpainting.*

   By discerning objects in both an XRF and the surface painting and comparing these, objects of the XRF that belong to the surface layer are identified. The remaining areas of the XRF (i.e. those that couldn’t be matched with the surface painting) are assumed to belong to the hidden painting. The example-based inpainting algorithm of Criminisi et al. [8] is applied to the image containing only these hidden regions to obtain the reconstructed XRF.

2. *Chapter 5 has shown that a colour image can be constructed from XRF images using classification based on an example image.*

   A training set consisting of chemical compositions of known colours is constructed from the example painting by performing XRF point measurements or by estimating the chemical values. Then, the actual XRF data is classified such that each pixel is assigned a colour based on its chemical composition. The classification is done with a nearest-neighbour classifier: for each chemical composition the most similar example compositions are determined and the colour that appears most frequent among these samples is assigned to the pixel.

Quantitative results and visual inspection indicated that the first method identified most of the XRF pixels correctly (approx. 87% of all pixels). This suggests that it is able to produce a fair reconstruction of the XRF of the hidden painting.
The colourization stage was evaluated using only visual inspection since the actual colours are unknown. Examination of reconstructions obtained with two different example paintings suggested that the performance was consistent. Moreover, in both cases the colourizations were found to correspond well with the expected colours.

A virtual reconstruction can be very valuable for art historians since the hidden painting might otherwise never become visible. This would be a loss since the buried compositions are often of great art historical value.

6.2 Discussion and future research

This thesis has provided a good starting point for virtual reconstruction of hidden paintings based on XRF images. It has become clear that there are a lot of factors involved and that the reconstruction is a complex issue. This section addresses the difficulties, especially with regard to future research.

There are in total five main processes in the current procedure that could be investigated more thoroughly. They are already discussed chapter 4 and 5; the most important issues are presented here.

Object detection
To find the objects in an XRF or in the surface painting, the image in question is divided into several slices. The number of slices affects the uniformity of the values comprised within an object. Future research may examine the optimal number of slices: how uniform should the values be to consider them as a single object?

For each slice, its objects are found by looking for connected pixels. It may however be worthwhile to investigate whether object could be found directly in an XRF or in the surface painting, for example using edge detection.

Object matching
The objects retrieved from the XRFs and the surface painting are compared to determine which XRF-objects correspond to the surface painting. Currently, the objects are compared as a whole but partial matching could also be used. It may improve results since objects of the XRF do not always appear as a whole on the surface painting.

Inpainting
In this study, the inpainting method of Criminisi et al. [8] was used to fill in the regions of the XRF where the information did not correspond to the hidden painting. A preliminary study had shown that this method was expected to yield the best results [32]. However, future research may look into this topic more thoroughly and perform experiments with other inpainting procedures as well.

Acquiring training data
Two methods were discussed to obtain training data from an example inpainting: the chemical values could either be obtained by performing XRF point measurements or by estimation. The first option is preferred since it provides the most accurate values. Future research should therefore focus on this approach. Here, it is important to make sure enough point measurements are available and that the analyses provide precise chemical values and colours of the selected points.
The advantage of the second method is that it in general yields more training samples since the chemical values of all pixels of the example image are available. This option may therefore be studied thoroughly as well such that the estimation of chemical values becomes more reliable.

**Classifier design**

The classification approach used in this study is template matching, implemented with the nearest-neighbour classifier. Although this provides a good starting point, future research may look into the use of other, more complex classifiers.

In addition, the optimal number of neighbours was unclear: in case of *Patch of Grass*, five neighbours was most often found as the best number but three, seven and nine were suggested by the cross-validation as well. Therefore, this issue should be re-examined in future research when more/other data becomes available.

This study has shown that the colours of the virtual reconstruction are difficult to retrieve (if at all) from the XRF data itself. An important limitation in this study was the lack of chemical and artistic knowledge: linking the chemical elements to certain colours requires expert knowledge on the composition of pigments, the use of pigments by the artist, etc.. Future research could therefore investigate this more thoroughly by cooperation with other experts, in particular from the field of art and/or chemistry.

The example image plays a crucial role in the reconstruction method presented in this thesis since it determines the colours that are used in the virtual reconstruction. Although guidelines for choosing an appropriate example are given in this study, it would be worthwhile to address this issue in future research in more detail.

Moreover, future research may investigate how the current research could be extended to use multiple examples. Since finding an appropriate example may be difficult, it could be useful when the reconstruction method can use information from different examples.
References


REFERENCES


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Glossary

(Blind) Source Separation Source separation techniques try to extract the underlying sources of mixtures of two or more signals. When this is done using little to no information about the sources, it is called Blind Source Separation. (page 18)

Classification Classification is a task of pattern recognition: a certain pattern is recognized as being part of a special class of patterns. A pattern is classified when it has been assigned to a certain class. (page 40)

Colour map A colour map is table or matrix in which for a number of labels a certain colour is stored. (page 42)

Colour quantization This technique is used to reduce the colours of an image: instead of many different colours, only a few representative colours are used. (page 24)

Colourization Colourization refers to the procedure where a greyscale image is converted to a colour image. This can be done using example images (i.e. example-based methods) or colour scribbled supplied by the user (i.e. scribble-based methods). (page 36)

Dataset Most often a dataset is a matrix where the rows correspond to the observations and the columns to the variables or features. (page 41)

Elemental distribution map See XRF map or image. (page 7)

Euclidean distance The Euclidean distance or Euclidean metric is the 'ordinary' distance between two points that one would measure with a ruler, and is given by the Pythagorean formula. (page 43)

Feature space When patterns are represented in terms of d features (i.e. with a vector of numbers), then they can be viewed as a point in a d-dimensional space. This space is called the feature space. (page 43)

Feature vector The feature vector of an object is a vector holding numerical values for some characteristics of the object, such as its size. (page 26)

Hg Hg is the chemical symbol for mercury. When it is found as part of a pigment, the pigment is most often Vermilion; a red colour. (page 15)

Hidden painting Hidden paintings are paintings that are fully covered by another painting (called surface painting) such that they aren’t visible to the naked eye any more (page 3)
<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image segmentation</td>
<td>Image segmentation is a technique that separates the pixels of an image into distinct regions. The regions can be separated based on certain characteristics, depending on the application and chosen algorithm. (page 21)</td>
</tr>
<tr>
<td>Infrared Reflectography (IR)</td>
<td>Infrared Reflectography records the infrared light that an object emits using a camera adapted to receive infrared radiation. (page 5)</td>
</tr>
<tr>
<td>Inpainting</td>
<td>The term inpainting is used to denote the procedure to fill in missing regions in an image. There are many alternative terms used in literature, such as 'image completion' and 'image interpolation'. (page 30)</td>
</tr>
<tr>
<td>k-Neighbourhood of pixel</td>
<td>The pixel neighbourhood is also known as the 'window'. It is the collection of pixels that surround the pixel. (page 23)</td>
</tr>
<tr>
<td>Luminance</td>
<td>Luminance is an indicator of how bright a surface appears. In a greyscale image, the luminance of a pixel is just its pixel value: the whiter the pixel, the higher its value and the higher its luminance. (page 38)</td>
</tr>
<tr>
<td>Nearest-neighbour approach</td>
<td>A nearest-neighbour classifier assigns the label which is most frequent among the training samples nearest to the new pattern; when the most nearest label is applied directly, it is a one nearest-neighbour classifier (1-NN). (page 43)</td>
</tr>
<tr>
<td>Old Master painting</td>
<td>The term 'Old Master' in general denotes a European painter of skill who worked approximately from the 13th to the 16th or 17th century. Examples of well-known Old Masters are Leonardo da Vinci, Raphael, Pieter Bruegel the Elder and Rembrandt van Rijn. (page 1)</td>
</tr>
<tr>
<td>Pigment</td>
<td>The colouring substance of a paint. These are chemical compounds that selectively absorb certain wavelengths of light. Examples are Vermilion (red), Naples Yellow (yellowish white) and Cobalt Blue (blue). (page 15)</td>
</tr>
<tr>
<td>Point measurements</td>
<td>Analyses of only selected points of an object. (page 9)</td>
</tr>
<tr>
<td>Principle Component Analysis</td>
<td>PCA is a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. The first component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. (page 11)</td>
</tr>
<tr>
<td>Sb</td>
<td>Sb is the chemical symbol for antimony. There are a number of pigments that contain antimony, one example is Naples Yellow (yellowish white). (page 15)</td>
</tr>
<tr>
<td>Shape descriptor</td>
<td>A shape descriptor is used to represent a shape or object by its characteristics. These characteristics can then be used to assess the similarity between different shapes. (page 25)</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Shape matching</td>
<td>Shape matching is a technique that is used to measure the similarity between shapes. For this, the shape should be described by some shape descriptor and a similarity measure along with a threshold is required.</td>
</tr>
<tr>
<td>Similarity measure</td>
<td>As the name implies, a similarity measure is a measure that is used to assess the similarity between two objects. When the objects are represented by numerical values, a distance measure can be used.</td>
</tr>
<tr>
<td>Slices</td>
<td>The term 'slice' refers in this study to an image that contains only those pixels of an image that have a value within a specified range. These pixels will appear white and the remaining pixels as black.</td>
</tr>
<tr>
<td>Surface painting</td>
<td>The painting that is visible to the naked eye is called the surface painting.</td>
</tr>
<tr>
<td>Template matching</td>
<td>The most simple approach to classification is template matching. Here, a new pattern is assigned to the class of which the template pattern is most similar to the new pattern.</td>
</tr>
<tr>
<td>Thresholding</td>
<td>Thresholding is a technique often applied in image processing to divide the pixels into groups: those that have a value lower than the threshold and those that have a value equal or higher than the threshold.</td>
</tr>
<tr>
<td>Training set</td>
<td>A dataset of labelled patterns that is used to train a classifier is called a training set. It is used to 'learn' which kind of patterns correspond to which class.</td>
</tr>
<tr>
<td>X-Radiography (XR)</td>
<td>In this technique X-Rays are directed through a sample such that they darken the photographic plate placed behind the sample wherever the radiation is not absorbed.</td>
</tr>
<tr>
<td>XRF</td>
<td>The abbreviation 'XRF' stands for X-Ray Fluorescence Spectroscopy, a technique used to examine the chemical composition of a sample. However, in this study it is often used to denote the XRF map or image; the meaning will be clear from the context.</td>
</tr>
<tr>
<td>XRF map or image</td>
<td>The term XRF map or XRF image refers to the image that shows the concentration of a specific chemical element in a region: white indicates a high concentration whereas black corresponds to a low intensity.</td>
</tr>
<tr>
<td>Z-value</td>
<td>The Z-value is the atomic number of the chemical element in the periodic system.</td>
</tr>
</tbody>
</table>
Appendix A  Search methodology: key words and results

This appendix addresses the search methodology that is used to find the literature presented in section 2.3 and chapter 3. A set of key words is determined first, after which synonyms are added to obtain more studies. Finally, the results are examined and the most important researches are selected.

To find literature about virtual reconstruction of hidden paintings using XRF images\(^1\) a set of key words is determined as follows:

\[
\begin{align*}
\textit{topic: } & \text{ virtual reconstruction of hidden paintings using XRF images} \\
\textit{key words: } & \text{ virtual - reconstruction - hidden - painting - xrf}
\end{align*}
\]

Of course, many queries can be made with these words, each with a different combination of a different subset of the key words. However, queries with only 1 or 2 key words are expected to retrieve too many general sources: they will yield sources that only slightly cover the topic of this research. Therefore, the initial list of queries consists of combinations of 3 key words, as shown in table A.1.

For each query (i.e. combination of key words), its relevance is determined. The relevance depends on the key words: some are more important than others. For example, the key word 'hidden' is very important (this research is not about visualizing any painting) but if 'xrf' in included, this also indicates that the research looks 'beyond' the surface of an object. In addition, researches about visualizing not a painting from an XRF but something else that is hidden, are relevant as well.

From the initial list of queries, a second list is made. This list (shown in figure A.1), adds synonyms to the queries that had a high relevance score. The synonyms used are the following:

- virtual = digital
- reconstruction = visualization (these are not really synonyms but for the search both key words are relevant)
- hidden == buried = covered
- For 'painting' no true synonym is available (studies on for instance murals or frescoes will be found by leaving out this key word).
- xrf = 'x-ray fluorescence'

The table shown in figure A.1 shows that in total 46 documents were found but 32 documents remained after removing duplicates. The title, abstract, authors and sources were examined to select truly relevant studies: when they investigated some form of hidden layer they are discussed in chapter 3 and when they merely give a good impression of how XRF can be applied in art analysis they are addressed in section 2.3.

\(^1\)The focus is on XRF images because they are expected to yield the best view on the hidden painting (see section 2.2).
### Table A.1: Set of queries constructed to find literature on virtual reconstruction of a hidden painting, using XRF images. Note that the words are connected using ‘AND’.

<table>
<thead>
<tr>
<th>nr.</th>
<th>Keywords</th>
<th>Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>hidden painting xrf</td>
<td>++</td>
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**Figure A.1:** Second set of queries constructed to find literature on virtual reconstruction of a hidden painting, using XRF images. This set consists of the most relevant queries from table A.1 and their synonyms. Note that the words are connected using ‘AND’. Some queries yield two numbers of results due to difference in spelling: visualization vs. visualisation.
Appendix B Painting and pigments

This appendix provides some background information on the artistic aspects of this study. First, section B.1 addresses the paint and its components used by an artist. Several types of pigments and their (chemical) composition are described in section B.2.

The following sources are used for this chapter. They are listed here because they do not contribute to specific sections.

- The text book ‘Het Schilderij: materiaal techniek-behoud’ by Knut Nicolaus [31]
- The WebExhibit on pigments by the Institute for Dynamic Educational Advancement [19] which refers itself to numerous validated sources
- Infrared spectra of paints and coatings found by the Testing Centre of the Faculty of Physics and Chemistry, University of Tartu [42]
- Several pages from Wikipedia [47].

It should be noted that the last source (Wikipedia) generally cannot be seen as valid source to build on. In this case however, the information is only used to gain elementary understanding and give basic descriptions.

B.1 Components of paint

The paint used in old paintings (and in many new ones too) is made by the artists themselves. It is constructed from a pigment and a binder:

- **Pigments** are granular solids incorporated into the paint to contribute colour. They are materials that change the colour of light it reflects as the result of selective colour absorption. When white light (a roughly equal mixture of the entire visible spectrum of light) reaches a pigment, some wavelengths are absorbed by the chemical elements of the pigment, and others are reflected. This new reflected light spectrum creates the appearance of a colour.

- Pigments need a special **binder** to bind the pigments together and onto the surface. The pigment is not soluble in the binder, in contrast with a dye (which is soluble such that mixing it with a binder results in a suspension).

  The binder strongly influences properties as gloss potential, exterior durability, flexibility, and toughness. Examples of binders are synthetic or natural resins such as acrylics, polyurethanes, polyesters, melamine resins, epoxy, or oils.

To make paint, the dry pigment is first ground with mortar and pestle (vijzel in Dutch) and then mixed with water or oil by ‘rubbing’ it together on a plate of stone (e.g. marble) or glass. Some pigments can be rubbed longer than others: the colour of Vermilion only improves when rubbed for a long time, while Lead-tin Yellow loses its colour when rubbed too fine.
B.2 Pigments: their colours and chemical composition

The Old Masters could use natural inorganic, artificial inorganic or natural organic pigments for their paintings. The first category consists mainly of earth colours such as Red Ochre and Umber but also of pigments using minerals such as Ultramarine (made with lapis lazuli) and Azurite. Lead White, Vermilion and Copper Green are made artificially. The natural organic pigments are made from animal or botanical products, for example berries, carrots, coloured types of wood and small animals. The black colours belong to the organic pigments as well.

Some of the pigments used most often in old paintings are discussed in section B.2.1 to B.2.7, categorised according to the colours they produce.

B.2.1 White pigments

Lead White is historically, artistically and scientifically the most important pigment. It is mentioned in all technical art sources and paint recipes since ancient history.

Until the 19th century this was the only white paint used in the paintings. Other white pigments such as Zinc White and Titanium White that are nowadays also used, weren’t applied by artists until 1840 and 1918 respectively.

Lead White was mixed with almost all colours to make them lighter. It was also used as a base layer for the painting. One reason for doing this was that Lead White, mixed with oil, dries quickly.

When mixed with Vermilion or Black, Red or Yellow Earth, Lead White was used for skin colours; the colour of the sky is produced by mixing with Azurite or Ultramarine. The white shirt, cloths, blouses and big white collars of the Dutch and Flemish paintings consist of Lead White, occasionally mixed with chalk (calcium carbonate).

Chemical structure
As the name implies, the most important chemical element in Lead White is lead. The formula of lead white is $2\text{PbCO}_3\text{Pb(OH)}_2$: it contains ordinarily about 70% of lead carbonate and 30% lead hydrate.

B.2.2 Yellow pigments

The most important yellow pigments are Lead-tin Yellow, King’s Yellow (Orpiment), Naples’ Yellow and Yellow Ochre (see figure B.1).

![Figure B.1: Lead-tin Yellow (A), King’s Yellow (B), Naples’ Yellow (C) and Yellow Ochre (D).](image)

Lead-tin Yellow was an important pigment. It is a granular, lemon yellow pigment that can mostly be found on paintings from the 15th, 16th and 17th century. Before that time it wasn’t used very often and in the 17th century it was gradually replaced by Massicot and Naples Yellow. Because of this, Lead-tin Yellow was often mistakenly identified as one of those new pigments. Only in 1940/41 it was rediscovered by Richard Jacobi from the Doerner Institute at Munich and reconstructed from old recipes.
Chapter B: Painting and pigments

... Chemical structure
The formula for Lead-tin yellow is $Pb_2SnO_4$: not surprisingly it contains lead and tin.

**King’s Yellow or Orpiment** is a 'hell yellow' colour. It is mostly found on panel paintings from the 12th and 13th century, and less in older paintings. The lack of use is probably not due to the toxic nature of the pigment but to the fact that it dries very slowly. It is also difficult to mix King’s Yellow with other colours.

... Chemical structure
King’s Yellow is yellow arsenic sulfide: $As_2S_3$.

**Naples Yellow** can range from a somewhat muted, or earthy, reddish yellow colour to a bright light yellow. The Old Masters used this pigment frequently in their paintings.

It is one of the oldest synthetic pigments, dating from around 1620, and was used well into the 20th century. However, Chromate Yellow and Cadmium Yellow became available around 1820 and 1850 respectively and replaced the Naples Yellow.

... Chemical structure
Naples Yellow consists of lead combined with antimony. The formula is: $Pb(SbO_3)_2$ or $Pb(SbO_4)_2$

**Ochre**, including all shadings, is one of the oldest and most used pigment. It can be seen all over Europe and was already used in prehistoric cave paintings. Ochres vary widely in transparency; some are quite opaque, while others are valued for their use as glazes.

... Chemical structure
Ochre contains iron (it might therefore resemble the colour of rust). The formula is $Fe_2O_3H_2O$.

### B.2.3 Blue pigments

The most used blue pigments are shown in figure B.2. They are described below.

![Figure B.2: Ultramarine (A), Azurite (B), Indigo (C), Smalt (D) and Prussian Blue (E).](image)

**Ultramarine**, the most beautiful blue pigment, was as expensive as gold. It was made from the Asian semi-precious stone lapis lazuli and mainly imported through Venice.

It was used from the 14th to the middle of the 15th century, mainly by Italian painters. The scarcity and the difficult and time-consuming production made it too costly for many painters however.

When Ultramarine is mixed with oil, a dark, almost black blue is obtained. To compensate, painters added a white or light blue layer underneath the Ultramarine such that light was reflected. Sometimes the Ultramarine was directly mixed with Lead White.

Ultramarine was not mixed with other colours than Lead White, except for other shades of
blue and organic red pigments. The latter were used to obtain purple shades, since Ultramarine with its violet undertone was more suitable for this than the more greenish Azurite.

*** Chemical structure
Ultramarine is a complex sulphur, containing sodium aluminium silicate. The formula is $Na_{8-10}Al_{6}Si_{6}O_{24}S_{2-4}$.

Azurite was often used instead of Ultramarine to reduce costs. Especially in bigger paintings Azurite was used, or Azurite covered with a thin layer of Ultramarine. Azurite (in contrast with Ultramarine) is known from ancient times and was used until the 18th century. In the 17th century it became less popular and in the 18th century it was replaced by Prussian Blue, which was then discovered.

*** Chemical structure
The formula for Azurite is $2CuCO_3Cu(OH)_2$. It is a basic copper(II)-carbonate.

Indigo is another alternative for Ultramarine to paint blue. This blue botanical paint base was used during all periods of the European art history. It was made from the East-Indian indigo plant and imported in great amounts since the 16th century.

*** Chemical structure
The chemical name for Indigo is $2,2' - Biindolinyliden - 3,3' - dion$. It consists of carbon, oxygen, hydrogen and nitrogen molecules.

Smalt, consisting of finely ground glass which is made blue with cobalt, was the earliest of the cobalt pigments. The size of the grain determines the intensity of the colour: when the pigment is ground too much, the colour turns pale.

Smalt can be seen quite frequently on paintings from the 16th, 17th and 18th century. For example, Rubens (1577-1640) used this pigment very often but diluted with oil, possibly containing resin. This resin fixated the pigment after the oil was evaporated. Further adding of for instance Lead White sped up the drying process.

Cobalt has been used to produce blue glass in ancient times and in the 15th century Venice. The discovery of using Cobalt as pigment is assumed to be made in the middle of the 16th century. However, the pigment is already found on paintings from the 15th century, for example on an altar by Michael Pacher (c.1435-1498).

*** Chemical structure
Smalt contains potassium ($kalium$ in Dutch), cobalt and silicate (glass). It can be made by heating quartz, potassium carbonate and small amount of cobalt(II)-chloride to 115°C and inserting the hot product into cold water. The disintegrated glass must then homogenized in a mortar.

Prussian Blue is one of the first synthetic pigments, discovered by accident in Berlin in 1704. Colourmaker Diesbach made the blue pigment accidentally when experimenting with the oxidation of iron.

The pigment was available to artists by 1724 and was extremely popular throughout the three centuries since its discovery. Its name comes from the fact that it was first extensively used to dye the dark blue uniforms of the Prussian army.
Chemical structure

The composition of Prussian blue was uncertain until recently. One of the reasons is that even pure Prussian blue is structurally complex. The formula is $Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$.

### B.2.4 Green pigments

The Old Masters did not have a pure, clear and yet opaque green. The intense green colours visible on paintings from the 13th to mid-16th century, consist most often of a mixture of Copper Green, Lead White and/or Copper-tin Yellow. In the 17th and 18th century, Copper Green appears to have been applied as top layer on Green Earth. Swatches of the green pigments can be seen in figure B.3.

![Figure B.3: Verdigris (A), Green Earth (B) and Malachite (C).](image)

**Copper Green or Verdigris** was the most vibrant green pigment available until the 19th century and frequently used in painting. Because of its transparency, Verdigris was often mixed with, or glazed over Lead White or Lead-tin Yellow.

Verdigris is lightfast in oil paint, as numerous examples of 15th century paintings show. However, its lightfastness and air resistance is very low in other media.

Chemical structure

Verdigris consists of a copper acetates, ranging in colour from green to blue. Neutral verdigris is $Cu(CH_3COO)_2H_2O$, and basic Verdigris contains more $Cu(OH)_2$ and $H_2O$.

**Green earth** has been known as a pigment since ancient times. The colour depends on the point of origin: cool, soft shades are named 'Veronese Green Earth' and warm, somewhat brownish shades are called 'Bohemian Green Earth'.

In early-Italian paintings the Green Earth was used as underpainting for the red parts such as faces and hands.

Chemical structure

Green Earth has complex structure, consisting of aluminosilicate minerals. The formula is $K[(Al,Fe^{III}),(Fe^{II},Mg)](AlSi_3, Si_4)O_{10}(OH)_2$.

**Malachite** is another pigment used by painters for the colour green. Its use can be traced back to ancient times but it was not frequently applied on paintings. The pigment can be found on some paintings from the Flemish School.

Chemical structure

Malachite is chemically similar to the blue pigment Azurite. The formula is $2CuCO_3Cu(OH)_2$.

**Copper Resinate** was believed to have been used often as green pigment. However, in 2005 art historian dr. Margriet van Eikema Hommes found that this is not true. After thorough analysis of old recipes and new laboratory results, it appeared that not a mixture of Verdigris...
and hot varnish (resulting in Copper Resinate) produced the green colour, but a mixture of Verdigris with cold oil or varnish.

The original bluish green tint of the copper fades to brown in the course of time, which means that once intense blue-green colours now appear much ‘warmer’. Painters must have been aware of this, since this process is already mentioned in old documentation. In addition, Leonardo da Vinci advised to varnish Copper Green immediately after application because the contact with air causes it to turn brown as well.[-2mm]

Since Copper Resinate is a mixture of Verdigris and hot varnish, its chemical composition is very similar to that of Verdigris: \( Cu(C_{19}H_{29}COO)_2 \).

### B.2.5 Red pigments

The most common red pigments are shown in figure B.4. The description follows below.

![Vermilion, Red Ochre, Minium](image)

*Figure B.4: Vermilion (A), Red Ochre (B) and Minium (C).*

**Vermilion** is the most important red pigment: an opaque and clear pigment that is used in many paintings made before the 20th century. It can be found in nature but has been artificially made since centuries. Nowadays the pigment Cadmium Red is used instead.

*Chemical structure*

Chemically, the pigment is mercuric sulfide and like all mercury compounds it is toxic. The formula is \( HgS \).

**Earth pigments** were, beside Vermilion, the most used red paint bases. Red Ochre and Iron Oxide can appear as shades from matted red to dark red brown; among these there are a number of shades that show much resemblance with Vermilion.

*Chemical structure*

Red Ochre is an anhydrous iron(III)-oxide. The formula is \( Fe_2O_3 \).

**Minium**, also called Red Lead, is only found on a small number of paintings. It is on the other hand frequently found on Roman and early-Gothic sculptures, mostly as ground layer for Vermilion. Although old technical art sources mention it as possible pigment for the red shades of a painting, not much of it is found.

Painters often constructed red parts in the painting with different layers. Vermilion could be used as basic layer on top of which shades are made with the more ‘fierce red’ Minium. More intense, darker shades were obtained by covering the Vermilion with red wax.

*Chemical structure*

The formula for Minium is \( Pb_3O_4 \): is is a lead(II,IV)-oxide.
B.2.6 Brown pigments

Brown pigments are not much applied in paintings from the Middle Ages. Only since the 16th century are they used more frequently and in the 17th and 18th century they actually dominate the palette of much paintings.

Often, brown was made by mixing black, yellow, red and blue pigments but the most common brown colours are the natural earth shades of Brown Ochre and Umber. Also Van Dyck Brown was used. The three pigments are shown in figure B.5.

![Figure B.5: Brown Ochre (A), Umber (B) and Van Dyck Brown (C).](image)

**Brown Ochre** is yet another variation of Ochre (see yellow and red, sections B.2.2 and B.2.5 respectively). It is made from a natural mineral consisting of silica and clay owing its colour to iron oxide.

**Chemical structure**

As Red and Yellow Ochre, Brown Ochre is an anhydrous iron(III)-oxide. It is partially hydrated, resulting in the formula $Fe_2O_3(H_2O)$.

**Umber** is a greenish brown earth shade, similar to Ochre. It is also made from natural mineral found throughout the world, in many shades, in hues from yellow to brown, and faint blue. By burning, Umber can become a reddish dark brown.

**Chemical structure**

Umber is also an iron(III)-oxide but now containing manganese(IV)-oxide. The formula is $Fe_2O_3MnO_2$.

**Van Dyck Brown** is an 'earthy' brown coal which, when applied with oil, produces a dark brown colour. Until now this pigment has not been found on paintings made before the 17th century.

**Chemical structure**

Van Dyck Brown contains organic residues of decaying organic matter, such as soil, peat or brown coal.

B.2.7 Black pigments

For the production of black paint the Old Masters mostly used Vine Black, Bone Black or Soot.

**Vine Black** is a botanical black, traditionally produced by charring desiccated grape vines and stems. It is similar to charcoal and has a bluish colour. Grey tints that are made with white also have a bluish tinge.

**Bone Black** is blue-black in colour and fairly smooth in texture. It is made by charring animal bones in closed retorts; usually bones from glue stock, boiled to remove fat and glue, are used.
Soot could also be used as black pigment. It refers to the black, impure carbon particles resulting from the incomplete combustion of a hydrocarbon.

Chemical structure

All pigments used to make black paint consists of pure elemental carbon (C). For example, Bone Black contains about 10% carbon, 84% calcium phosphate and 6% calcium carbonate, resulting in the formula $C + Ca_3(PO_4)_2$.

It should be noted that black parts on a painting don’t always contain black pigments: they are sometimes mixed from dark blue (for example Indigo) and a red wax. The portrait art of the 16th and 17th century contain lots of black pigments however. The painted subjects wore mostly dark clothing according to the time’s fashion. These colours were put as black on the canvas and Lead White was then used to add lighter shades.

Black could also be used as ground layer. In the Middle Ages for example, black or dark grey was used as ground layer for Azurite, increasing the intensity of the blue. In turn, since the black pigment dried badly when mixed with oil, painters often added an extra component, such as Copper Green.