Development of Scanning macro-XRF for the Investigation of Historical Paintings

Joint PhD thesis for award of the title Doctor in de wetenschappen: chemie and Doktor der Naturwissenschaften (Dr. rer. nat.) at the University of Antwerp and the University of Hamburg.

Matthias Wilhelm Emil Michael Alfeld

2013

Supervisor
University of Antwerp
Faculty of Science
Department of Chemistry
Prof. Dr. Koen Janssens

Supervisor
University of Hamburg
Faculty of Mathematics, Informatics and Natural Sciences
Department of Chemistry
Prof. Dr. José A. C. Broekaert
Front cover:

Holy Family with St. John the Baptist, after Caravaggio, private collection. The shown detail was acquired by means of Instrument C, operated at 50 kV and 1 mA with a step size of 0.25 mm and a dwell time of 0.2 s in 4 days. The elemental distribution images were colourized and superimposed with GIMP.
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I declare on oath that I completed this work on my own and that I have not used any but the mentioned sources. Neither this, nor a similar work, has been presented to a doctoral examination committee.

Ik verklaar op op eer en geweten dat ik deze thesis zelfstandig heb geschreven en geen andere dan de aangegeven hulpmiddelen en bronnen heb gebruikt. Ik verklaar verder dat dit proefschrift, of een gelijkaardig werk, nog niet werd voorgelegd aan een doctoraatscommissie/examencommissie.

Antwerp, 17.06.13
Acknowledgments

I would like to thank my parents and my sister for all the love and support they gave me through the years.

I thank my supervisors Prof. Dr. Koen Janssens and Prof. Dr. José A. C. Broekaert for their support and allowing me to pursue this rewarding topic for my PhD thesis. Also Prof. Dr. Piet Van Espen and Prof. Dr. Joris Dik are well remembered for their valuable advice and guidance throughout this project.

The members of the AXI²L research group of whom many became friends over the years offered valuable support, especially Dr. Geert Van der Snickt and my former Bachelor and Master student and current colleague Stijn Legrand and his family are well remembered. Also not to be forgotten are: Dr. Simone Cagno, Dr. Letizia Monico, Dr. Marie Radepont, Gert Nuyts, Wout De Nolf, Frederik Vanmeert, Stefano Barenghi, Kevin Helemans, Dr. Veerle van der Linden, Willemien Anaf, Joana Pedroso and Dr. Ana Cabal. So are the visiting students Alessandra Botteon, Samuela Bellodis, Luisa Favaretto and Elisa Longhini.

This work would not have been possible without the support of the technical and administrative staff of the University of Antwerp, most notably Nelly Suijkerbuijk, Noemi Van Alsenoy, Rene Corremans, Gilles Van Loon and Luc Geuens.

David Swetzoff made valuable contributions to this project and kept on pushing us to try what was believed just a few years ago not possible.

The results presented in this work were acquired in a number of international and interdisciplinary collaborations. Measurements at the Deutsches Elektronen Synchrotron were done in collaboration with Dr. Karen Appel, Dr. Gerald Falkenberg and Dr. Manuela Borchert. The experiments at the National Synchrotron Light Source were done in collaboration with Dr. D. Peter Siddons and Dr. Arthur Woll. During a stay at the Australian Synchrotron Dr. Chris Ryan, Dr. Darryl Howard and Dr. Robin Kirkham gave me valuable insight in their approach to XRF imaging with the Maia detector and the evaluation of XRF data. I also thank Dr. David Thurrowgood of the National Gallery of Victoria (Melbourne, Australia) for discussing the investigation of historical paintings with me.

The experiments in museums were performed and interpreted in close collaboration with painting conservators and art-historians employed at these and other institutions. I would like to thank without special order: Lizet Klaassen (Royal Museum of Fine Arts, Antwerp, Belgium), Griet
Steyaert (independent conservator, formerly at the Royal Museum of Fine Arts, Antwerp, Belgium), Petria Noble and Annelies van Loon both from the Royal Picture Gallery Mauritshuis (The Hague, The Netherlands), Anna Krekeler, Ige Verslype, Laurent Sozzani and Dr. Arie Wallert of the Rijksmuseum (Amsterdam, The Netherlands), Dr. Ella Hendriks and Dr. Teio Meedendorp of the Van Gogh Museum (Amsterdam, the Netherlands), Luuk van der Loeff (Kröller-Müller Museum, Otterlo, the Netherlands), Meta Chavannes (Stedelijk Museum, Amsterdam, the Netherlands, formerly at the Kröller-Müller Museum). The advice of Prof. Dr. Margriet van Eikema Hommes (Delft University of Technology, the Netherlands), Prof. Dr. Claudine Chavannes-Mazel (University of Amsterdam, the Netherlands) and Prof. Dr. Ernst van de Wetering (Rembrandt Research Project, Amsterdam, the Netherlands) is also highly valued.

I thank Claudia Laurenze-Landsberg of the Gemäldegalerie - Staatliche Museen zu Berlin (Germany), Dr. Andrea Denker of the Helmholtz-Zentrum Berlin (Germany) and Petria Noble (Royal Picture Gallery Mauritshuis, The Hague, The Netherlands) for their support in the acquisition and interpretation of the results presented in Chapter 5.

In connection with the investigation of Caravaggio’s paintings in Rome and Milan I would like to thank Dr. Marco Cardinali, Dr. M. Beatrice De Ruggieri and Dr. Matteo Positano of emmebi diagnostica artistica s.r.l. (Rome, Italy), and Prof. Dr. Bruno Brunetti (University of Perugia, Italy). Furthermore, I thank the Academica Belgica for the hospitality.

I thank Dr. Ina Reiche and Dr. Katharina Müller of the Laboratoire d'Archéologie Moléculaire et Structurale (LAMS) CNRS UPMC Univ Paris 06 (Paris, FR) and Dr. Myriam Eveno and Dr. Michel Menu of the C2RMF (Paris, FR) for their support in the confocal XRF measurements in Paris in January 2013.

In connection with the development of the M6 Jetstream I thank Dr. Michael Haschke, and Dr. Roald Tagle of Bruker Nano GmbH (Berlin, Germany) for considering my advice.

Concerning the introduction, I would like to express my gratitude to Dr. Vivi Tornari, Dr. John Delaney and Dr. Aurele Adam for their support. Further, I would like to thank the following persons for discussing their fields of expertise with me: Prof. Dr. Bernhard Blümich, Dr. Kaori Fukunaga, Dr. Michel Menu, Dr. Peter Reischig, Dr. Fauzia Albertin and Dr. Alessandro Re.

I thank the National Geographic Channel and Sullivan Entertainment for documenting part of this work in television documentations.
Finally, I thank my friends Alexander Kostenko, Alexandra Silinski, Jean Waucomont and Dr. Andrey Tsyganov for the company during the long weekends of the last years.

I thank the Research Foundation - Flanders (FWO) for granting me a Ph. D. fellowship and a travel grant for the Denver X-ray Conference 2012. I also acknowledge the support of European Microbeam Analysis Society (EMAS) to visit the 20th International Congress on X-Ray Optics and Microanalysis (ICXOM) in Karlsruhe (Germany) in 2009. I acknowledge the support of the European Community’s Seventh Framework Program (FP7/2007-2013) that supported under grant agreement No. 226716 several research stays at DESY.
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Abstract

Historical paintings can be considered as one of the most precious parts of humanity’s cultural heritage. They have been the subject of intensive scientific studies for decades. The aim of these studies is to gain insight in their creation process and to preserve them for coming generations. Various techniques have been applied to their study, but a method that allows for the acquisition of distribution images of elements present in surface and sub-surface layers was still missing.

Scanning macro-XRF (MA-XRF) fills this gap. In this technique a focused or collimated X-ray beam of typically a few hundred micrometres diameter is used to scan the surface of the painting. The X-ray fluorescence signals that are emitted by the painting upon irradiation are recorded by one or more energy dispersive detectors. Elemental distribution images are obtained by setting each pixel to a grey scale value corresponding to the intensity of the recorded fluorescence radiation. Due to the penetrative nature of the X-rays, the elemental maps allow to study the distribution of elements in the surface and sub-surface layers of a painting.

The first MA-XRF experiments were performed at synchrotron radiation sources. However, as the pigments in an historical painting are commonly present at a concentration level of several mass percent, also well designed X-ray tube based MA-XRF instruments allow paintings to be investigated at a reasonable pace (of the order of several pixels per second). Four mobile scanners based on X-ray tubes were constructed in the course of this work. The most recent instrument allows to scan areas of 60 x 60 cm in 20 hours with a lateral resolution of 1 mm, while the best lateral resolution obtainable is 50 μm.

The value of these scanners is demonstrated in a number of case studies on historical paintings originating from the 16th to 19th century by important artists, such as Rembrandt van Rijn, Vincent van Gogh and Caravaggio. Different problems were addressed:

- Modifications to the painting’s original concept during its creation (pentimenti) can be visualized to gain insight in the artist’s modus operandi.
- Details of discarded and overpainted representations can be made visible again. X-ray radiography investigations can detect the presence of such depictions, but often fail at providing sufficient details for their interpretation.
- Non-original additions to a painting can be identified to allow for a better planning of conservation treatments.
The pigment use of an artist can be studied in detail, beyond what is possible by spot analysis.

Before the development of MA-XRF, Neutron Activation Autoradiography (NAAR) was the only technique that allowed for the acquisition of element specific images of historical paintings. Its capabilities are compared to that of MA-XRF in a case study on Govert Flinck’s “Portrait of Rembrandt”.

The results acquired by these in-house built scanners found general acceptance in the painting’s conservation and art-historical community; this prompted Bruker Nano GmbH (Berlin, Germany) to build a commercially MA-XRF scanner for the investigation of large flat objects. The instrument was based on the technical know-how of Bruker Nano GmbH in the design of XRF scanners and the experience obtained with the in-house built scanners of the University of Antwerp. The instrument, baptized M6 Jetstream, features spectrometric figures-of-merit comparable to that of the in-house built scanners.

The evaluation of XRF spectra is conventionally done by least squares fitting of individual XRF spectra. This approach became impractical as the pace at which data could be acquired became faster than that at which data could be processed. To accelerate the data processing, a software package, called Datamuncher, was written. The Datamuncher package allows for the processing of several thousand spectra per second based on Dynamic Analysis.

Paintings are layered structures and the MA-XRF distribution images of elements that are present in sub-surface layers contain absorption artefacts resulting from covering layers. Based on the fundamental parameter approach, it was investigated how these artefacts can be removed to enhance the readability or exploited to gain insight in the stratigraphy of the painting.

This work has considerably extended the range of scientific techniques available for the investigation of historical paintings.
Zusammenfassung

Historische Gemälde sind ein zentraler Bestandteil des kulturellen Erbes der Menschheit. Ihre Erforschung aber auch ihr Erhalt für kommende Generationen wird durch die Untersuchung mittels wissenschaftlicher Methoden unterstützt. Allerdings war bis vor kurzem keine Methode verfügbar, die es erlaubte Verteilungsbilder chemischer Elemente aufzunehmen, die sich auf und unter der Oberfläche von historischen Gemälden befinden.


Die ersten MA-RFA Messungen wurden an Synchrotron Strahlungsquellen durchgeführt. Allerdings wurde schnell klar, dass auch sorgfältig konstruierte, auf Röntgenröhren basierende Instrumente die Aufnahme von Verteilungsbildern in akzeptabler Geschwindigkeit (mehreren Pixeln pro Sekunde) erlauben, da Pigmente in Gemälden im allgemein zu mehreren Massenprozent vorhanden sind.

In dieser Arbeit wurden auf Röntgenröhren basierende Instrumente entwickelt. Das am weitesten entwickelte Instrument erlaubt es den gesamten Bewegungsbereich seiner Motortische (60 x 60 cm) mit einer Pixelgröße von 1 mm innerhalb von 20 Stunden abzurastern. Die höchste mögliche Ortsauflösung ist 50 μm.

Der Wert von Verteilungsbildern chemischer Elemente wird einer Reihe von Fallstudien von historischen Gemälden bedeutender Künstler wie Rembrandt, Vincent van Gogh und Caravaggio gezeigt. Verschiedene Fragestellungen wurden dabei untersucht:

- Es wurde gezeigt das Veränderungen am ursprünglichen Konzept des Gemäldes (so genannte Pentimenti) sichtbar gemacht werden können, was einen Einblick in die Arbeitsweise des Künstlers erlaubt.
Zusammenfassung

- Später zu einem Gemälde hinzugefügte Farbschichten können sicher identifiziert werden, was die Planung von Restaurationsmaßnahmen unterstützt.
- Der Pigmentgebrauch eines Künstlers kann genauer untersucht werden als es mit Punktmessungen möglich ist.

Vor der Entwicklung der MA-RFA war die einzige Methode, die es erlaubte Bilder zu erhalten, die die Verteilung chemischer Elemente andeuten, Neutronen-Aktivierungs-Autoradiographie (NAAR). Die Möglichkeiten von NAAR and MA-RFA werden in einer Fallstudie zu Govert Flincks „Porträt Rembrandts“ kritisch verglichen.

Das die Ergebnisse, die mit den an der Universität Antwerpen gebauten Instrumenten erreicht wurden, von Restauratoren und Kunsthistorikern gut aufgenommen wurden, überzeugte die Bruker Nano GmbH (Berlin) einen kommerziellen MA-RFA Scanner zu entwickeln. Der Scanner, M6 Jetstream genannt, basierte auf dem Wissen von Bruker Nano GmbH über die Entwicklung von RFA Scannern und der Erfahrung der Universität Antwerpen mit der Untersuchung historischer Gemälde mittels MA-RFA. Der M6 Jetstream erreicht vergleichbare analytische Güteziffern wie die an der Universität Antwerpen gebauten Instrumente.

RFA Spektren werden gewöhnlich ausgewertet indem mittels spezialisierter Software Paketen nach der Methode der kleinsten Quadrate ein Model des Spektrums an das gemessene Spektrum angepasst wird. Dieser Ansatz wurde auch zu Beginn dieser Arbeit verfolgt, erwies sich allerdings bald als unpraktisch da unter günstigen Umständen Daten schneller aufgenommen werden können als mit herkömmlichen Methoden ausgewertet.

Um die Datenauswertung zu beschleunigen wurde ein Software Paket mit dem Namen Datamuncher geschrieben das es erlaubt, basierend auf Dynamic Analysis, mehr als tausend Spektren pro Sekunde auszuwerten.


Diese Arbeit hat einen wertvollen Beitrag geleistet um die Methoden die für die Untersuchung von Gemälden zur Verfügung stehen zu erweitern.
Samenvatting

Historische schilderijen kunnen beschouwd worden als het meest kostbare aspect van het cultureel erfgoed. Reeds jaren zijn deze werken het onderwerp van doorgedreven wetenschappelijk onderzoek om een beter beeld te verkrijgen over hun ontstaansproces en om ze optimaal te bewaren voor de toekomstige generaties. Hoewel reeds een groot aantal technieken wordt aangewend voor deze onderzoeken, was er tot voor kort geen methode beschikbaar die het mogelijk maakt om distributiebeelden op te tekenen van elementen, die aanwezig zijn aan en net onder het oppervlak.

Deze leemte wordt opgevuld door de scanning macro-XRF techniek (MA-XRF). Deze techniek maakt gebruik van een gefocuseerde of gecollimeerde X-stralenbundel met een diameter van enkele honderden micrometer om het oppervlak van een schilderij af te tasten. De hierdoor in het kunstwerk ontstane X-straal fluorescentie signalen worden geregistreerd in één of meerdere energie dispersieve detectoren. Na de meting worden element specifieke verdelingsbeelden bekomen door aan ieder beeldpunt een grijswaarde toe te kennen die evenredig is met de intensiteit van de gemeten fluorescentiestraling. Dankzij het penetrerende karakter van X-straling, laten de element specifieke verdelingsbeelden toe om naast aan het oppervlak liggende verflagen, ook dieper gelegen lagen te bestuderen.

De eerste MA-XRF experimenten werden uitgevoerd aan synchrotron faciliteiten. Aangezien pigmenten in historische schilderijen vaak in concentraties van meerdere massapercenten aanwezig zijn, is het mogelijk om met een goed ontworpen MA-XRF toestel, gebruikmakend van een X-straalbuis als stralingsbron, schilderijen te onderzoeken aan een aanvaardbare scansnelheid van meerdere punten per seconde. Gedurende dit werk werden vier, op X-straalbuizen gebaseerde, mobiele scanopstellingen ontwikkeld. Het meest recente instrument staat toe om een gebied van 60 bij 60 cm af te scannen in een tijdspanne van 20 uur, met een stapgrootte van 1 mm. Dit toestel laat evenwel ook toe om metingen uit te voeren met fijnere laterale resoluties tot deze van 50 µm.

Met behulp van enkele case studies op historische schilderijen uit de 16e tot en met 19e eeuw van de hand van belangrijke kunstenaars zoals Rembrandt van Rijn, Vincent van Gogh en Caravaggio, worden de mogelijkheden van deze scanopstellingen aangetoond. Hierbij werden verschillende problemen bestudeerd:

- Verschillende aanpassingen die gedurende de ontwikkeling van het kunstwerk aan het originele concept aangebracht werden (pentimenti) kunnen in beeld gebracht worden met als gevolg dat het inzicht in de werkwijze van de kunstenaar verdiept kan worden.
- Details van verwijderde en overschilderde composities kunnen weer zichtbaar gemaakt worden. Ook via X-straal radiografieën kan de aanwezigheid van zulke aanpassingen gedetecteerd worden, maar beelden leveren vaak onvoldoende details op om de verborgen afbeeldingen correct te kunnen interpreteren.
- Latere en vaak niet-originele toevoegingen aan het schilderij kunnen geïdentificeerd worden, wat een betere planning voor toekomstige conservatie behandelingen toelaat.
- Het pigmentpalet van de kunstenaar kan in veel meer detail bestudeerd worden dan mogelijk is met behulp van punt analyses.

Voor de ontwikkeling van de MA-XRF scantechniek was neutronen activerings autoradiografie (NAAR) de enige techniek die het mogelijk maakte om element specifieke distributiebeelden op te tekenen van historische schilderijen. In het onderzoek op Govert Flincks “Portret van Rembrandt” werden de mogelijkheden van deze techniek vergeleken met deze van MA-XRF.

De conservatie- en kunsthistorische gemeenschap was zeer opgezet met de resultaten die bekomen werden met de zelfgebouwde scan-toestellen. Dit was voor Bruker Nano GmbH (Berlijn, Duitsland) het signaal om een commerciële MA-XRF scanner te ontwerpen die in staat is om grote vlakke voorwerpen te onderzoeken. Voor de bouw van dit instrument werd beroep gedaan op de technische kennis van Bruker nano GmbH in combinatie met de ervaring, opgedaan met de scanners die binnen de Universiteit Antwerpen ontwikkeld werden. Dit instrument werd “M6 Jetstream” gedoopt en is in staat om gelijkaardige resultaten te bekomen als de zelfgebouwde scanners.

In het algemeen wordt de interpretatie van XRF spectra uitgevoerd via een kleinste kwadraten fitting van de individuele XRF spectra. Deze werkwijze werd onbruikbaar doordat het opnemen van de data sneller verliep dan dat deze verwerkt kon worden. Om deze dataverwerking te versnellen, werd het “Datamuncher” softwarepakket geschreven. Dit pakket laat, gebaseerd op de Dynamic Analysis techniek, toe om enkele duizenden spectra per seconde te verwerken.

Schilderijen bestaan uit gelaagde structuren, waardoor de fluorescentiesignalen van elementen in dieper gelegen verflagen absorptie-verschijnselen ondergaan door de bovenliggende lagen, wat een invloed heeft op de resulterende MA-XRF verdelingsbeelden. Met behulp van de fundamentele parameterbenadering werd onderzocht hoe deze artefacten verwijderd kunnen worden uit de resultaten om de leesbaarheid van de beelden te verhogen of hoe deze gebruikt kunnen worden om een overzicht te bekomen van de verflagenstructuur.

Dit werk heeft de waaier aan wetenschappelijke technieken om historische schilderijen te onderzoeken gevoelig uitgebreid.
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1.1 Introduction

Historical paintings can be considered as one of the most precious parts of humanity’s cultural heritage. Although paintings have been executed on a wide range of supports and in various techniques, the most prominent ones are easel paintings (paintings on a portable support) executed in oil paint, such as the master pieces of Rembrandt van Rijn, Peter Paul Rubens, Caravaggio or Vincent van Gogh. These paintings are in the focus of this work.

Easel paintings have been the subject of intensive scientific studies for many decades. These investigations often focus on sub-surface layers to gain insight in a painting’s creation process, which allows studying the artist’s *modus operandi* and changes to the painting’s concept during its execution. Both can be important arguments in the attribution of a painting to an artist. An artist’s *modus operandi* determines how he prepared the support of his paintings, if and how he sketched his initial concept on the prepared ground, how he applied and manipulated the paint and which pigments he used. Easel paintings are created by superimposing layers of paint, often achieving optical effects by letting covered layers shine through thinly applied top layers. Thick paint layers are completely opaque, so that “repented” elements of a painting can be corrected by overpainting. These changes are called *pentimenti* (from the Italian verb *pentire*: “to repent”) and their identification and visualization, next to the visualization of the initial sketch, are key elements in the revelation of changes to the initial concept.

Further, paintings age and deteriorate with time, necessitating treatments to conserve them for coming generations. Also damages from improper handling or accidents need to be repaired. To plan such treatments the current state of the painting needs to be evaluated. This includes the identification of the materials used and an evaluation of the structural integrity of the painting. The earlier a defect is known, i.e. before it becomes visible on the surface, the better and easier it can be treated, sometimes just by adjusting storage conditions. In general as much of the paintings original structure as possible needs to be preserved. So it is of high importance to clearly discern between the paintings original structure and later additions, e.g. from previous restoration treatments.

The classical method of investigating a painting is visual inspection with different types of illumination and the aid of a stereomicroscope. This approach is in general limited to the surface, although in cracks of the surface sometimes hidden paint layers can be observed. In order to study the hidden layers and answer specific questions, sometimes samples from (preferably damaged) spots on the painting are taken. The decision if and
where samples are to be taken is preferably made after all available non-destructive means of investigation have been exploited. These samples are embedded in resin and polished to provide cross-sections through the painting’s stratigraphy. To preserve the painting’s original structure, the number of samples taken from a painting for scientific analysis has to be limited to a minimum [1].

Spectroscopic and spectrometric techniques develop rapidly, each couple of years doubling in performance and new methods are developed at an impressive rate [2]. These advanced analytical techniques also find application in the investigation of cultural heritage objects. A number of papers, commonly focusing on a single or small number of similar techniques, have been describing these applications [3-17]. Overviews dealing with established techniques for the analysis of easel paintings have also been subject of book chapters [1, 18].

In this chapter the imaging techniques available for the study of sub-surface layers in historical paintings and the role of scanning macro-XRF will be discussed. The focus will be on mobile instrumentation that can be installed in museums or galleries. This avoids the transport of easel paintings, which asks for considerable financial and logistic effort and exposes the painting to unnecessary stress from handling and changing climatic conditions.

While in-situ in its most narrow definition only describes techniques that can be applied to the painting on its normal resting place on the wall of a gallery or museum, here the term is extended to techniques that can be installed with reasonable effort in the conservation workshop of a museum.

Several techniques for the investigation of historical paintings necessitate large facilities, such as particle accelerators or nuclear research reactors. Particle Induced X-ray Emission (PIXE) is a suitable technique for the acquisition of (small) elemental distribution images. Dynamic PIXE, which is characterized by variations of the proton energy, allows for depth discrimination [19]. Several X-ray based techniques have been first applied at synchrotron radiation (SR) sources and later evolved into mobile instruments, including scanning macro-XRF. However, techniques such as X-ray Absorption Near Edge Structure (XANES) spectroscopy necessitate a monochromatic primary beam of high intensity and are limited to these sources [16].

These techniques are most often used for the analysis of samples taken from paintings, but several paintings have been brought to PIXE instruments for investigation [20-23]. Several examples of investigation of paintings by SR are given below.
For a long time the only method to acquire distribution images with an element specific character that are able to reveal underlying paint layers was Neutron Activation Auto-Radiography (NAAR) [24-26]. In NAAR transient radioactivity is induced in the painting by means of neutrons from a nuclear research reactor. Differences in radioisotope half-lives allow for the acquisition of autoradiographs dominated by different elements. NAAR is in detail compared to scanning macro-XRF in Chapter 5.

A number of imaging techniques only sensitive to the surface of paintings, such as multi-spectral imaging in the visible range [6] and Raman imaging [27] are omitted. Nonlinear imaging [28] is omitted, as currently too few case studies are available that allow to estimate the practical value of this technique for the investigation of historical paintings.

The fact that instruments suitable for in-situ investigations are commonly transportable allows using them not only in large museums, which have their own scientific department, but also in smaller ones. This approach has been realized in the MOLAB project [29]. The multi-technical approach for (spot) analysis of cultural heritage has also driven the development of specialized software [30].

1.1.1 The structure of easel paintings

![Schematic stratigraphy of an easel painting.](image)

Figure 1 Schematic stratigraphy of an easel painting.

The scientific investigations of easel paintings described in literature are in general focused on those created in the period from the Middle Ages to the end of the 19th century. A complete description of painting materials and techniques is far beyond the scope of this work, so that this text is limited to
a very general description, highlighting components relevant in the techniques and paintings discussed in this and the following chapters.

As seen in Figure 1 an easel painting consists typically of a support, one or more ground layers, paint layers and varnish that are applied on top of one another. Canvas and wooden panels are the most popular supports, but also other materials, such as thin copper plates, paper, stone, glass and even obsidian [31] are known. The material of the support has a significant influence on the applicability of transmission methods. Further, the preservation of the support is crucial to preserve the structure of a painting and its investigation can reveal key information on the painting’s history.

A canvas support is prepared by stretching it on a frame before applying the ground layer. This results in cusping, scalloping of the regular weave pattern along each stretched edge, which is preserved in the canvas structure after the ground has dried. The absence of a complete cusping pattern on all sides of the painting can indicate a later modification of the painting’s format [32]. However, if a large canvas was prepared and cut for the creation of several paintings, as it is typical for industrially prepared canvas, the absence of a cusping pattern is to be expected. The earliest possible date of a panel painting’s creation can be determined by dendrochronology of the support, if a characteristic year ring pattern can be observed in the accessible part of the panel.

The direct access to the painting’s support is often obstructed. Canvas loses its strength with time, so that it is sometimes stabilized by lining, i.e. gluing it on a second canvas, preventing direct observation of the canvas weave pattern, fibres and stamps on the back of the original canvas. Wooden panel supports were often stabilized by a wooden cradle fixed to their backside in order to reduce the expansion and shrinkage due to changed temperature and humidity that results in stress and cracks in the paint layers, obstructing the direct access to parts of the panel’s backside.

The surface of canvas is commonly sealed with a water based glue size, in order to protect it and prevent the absorption of the ground’s organic medium in the support. On the prepared support the first ground layer is applied. It provides a smooth surface to execute the painting on. The materials commonly used are chalk (CaCO₃), gypsum (CaSO₄·2H₂O), earth pigments and lead white (2PbCO₃·Pb(OH)₂) in glue or oil medium, but also quartz (SiO₂) has been found in 17th century paintings. While before the 16th century white grounds were common, later artists often used coloured grounds. The colour is achieved by the addition of pigments to the ground itself. In case of panel paintings, a similar effect can be achieved by the application of a second thin ground layer on the first ground, called
imprimatura, which also smoothes the surface of the ground. Coloured grounds, commonly of greyish to reddish colour, can be used in the mid-tones of the painting, either by being left exposed or allowed to shine through the surface paint layers. The ground layer is seldom subject to imaging experiments as it covers the entire support and can be easily studied in micro-samples taken from the edge of the painting.

Many artists sketch their initial concept directly on the ground of the painting. This is commonly done as an underdrawing, employing charcoal, chalk, metal point, ink or water-based black paint, or as an underpainting, defining main forms and principal shadows with brownish paint. The later was typical if a coloured ground was employed and contributed to the final appearance of the painting if covered by thin paint layers [33]. The sketch could either be made on the first ground or on the imprimatura.

The painting is built-up, following the initial concept laid down in the sketch, by superimposing paint layers on the ground. Paint consists of small particles of ground pigments in a polymerized organic medium. An overview of the pigments employed in the easel paintings investigated in this work is given in the next section.

Thin, translucent layers, containing next to pigments high amounts of organic binders were sometimes added as glazes on top of the paint layers to deepen colours and create shadows. The main pigments in a paint layer are commonly present at a concentration level of several mass percent.

As organic medium mainly drying oils (mostly linseed oil) sometimes with additions of natural resins for certain colours were used. But also water soluble media such as egg yolk, egg white, casein and Arabic gum are known in so called tempera paintings. In order to protect the painting and saturate the colours a varnish layer was added. Its investigation has been recently reviewed [4].

The organic binders become more stiff and brittle as they age. In combination with minor deformations of the support and mechanical stress from handling this can result in cracks in the paint layers and delaminations. In these areas the bond between two layers loosens and an air pocket is formed, which can results in the long term in loss of the paint layers. As such structural defects expand with time their detection and stabilization at an early stage is favourable.

1.1.2 Pigments
In Table 1 pigments used in historical paintings relevant to this work are given with their chemical composition and period of usage. Elements well
detectable by XRF are printed in bold, weakly detectable elements in italic. The focus is on pigments used in the period between 1400 and 1900, as the paintings described in this work originated from this period. The period of usage of a pigment is only specified if it was introduced or its usage discontinued in easel painting after 1400. This table is based on [34].

It has to be taken into account that pigments were named after their colour, mechanical properties and, if known, their origin. So, while a pigment’s name is often correlated to its chemical composition, it can also be ambiguous. Cinnabar and vermilion (both HgS) are chemically identical, strong red pigments. Albeit in the past both terms were used interchangeably, today the first term is used for the pigment yielded from the mineral cinnabar, while the latter refers to the synthesized pigment. Discrimination between the two based on MA-XRF is not possible and in the following only the term vermilion will be used. Also the term chrome green does in general not refer to chrome oxide greens, but to mixtures of yellow chromates (M\text{II}CrO\text{4}) with Prussian blue (Fe\text{III}[Fe\text{II}(CN)\text{6}]\text{−}) with different cations, yielding a green pigment.

Commercial pigments are also seldom pure in a chemical sense and can contain impurities and extenders.

It is worth noting that the palette used by European painters contains relatively few variations till the 19th century, when scientific progress made a broad range of new pigments available.

Lead-based whites (mainly 2PbCO\text{3}·Pb(OH)\text{2}) were the main white pigment for easel paintings available until the 19th century. Earth pigments (e.g. Ochres, Sienna and Umbra), mainly consisting of Fe and Mn oxides, were used to create brown, red and yellow tones. Black tones were usually created with bone black, lamp black, ivory black or soot whose colour results from carbon-based black, as does that of charcoal. Vermilion (HgS) was the most important red pigment. Blue was in general produced with smalt (ground Co rich glass), ultramarine (Na\text{7}Al\text{6}Si\text{6}O\text{24}S\text{3}), azurite (Cu\text{3}(CO\text{3})\text{2}(OH)\text{2}) or its synthetic equivalent blue verditer. Green pigments were malachite (Cu\text{2}CO\text{3}(OH)\text{2}), its synthetic equivalent green verditer and verdigris (Cu corrosion products, mainly acetates). Lead tin yellow (Pb\text{2}SnO\text{4}) was used until the 18th century, when it was replaced by Naples yellow (Pb\text{2}Sb\text{2}O\text{7}). Chalk (CaCO\text{3}) was used as an extender to paint, but was also used as a white pigment in a glue medium. Further, lake pigments were used. These are obtained by precipitating organic dyes on an inorganic substrate. An important example is red madder lake, derived from the roots of the Rubiaceae family, notably the Rubia tinctorum. Also yellow lake and blue indigo were used. These organic compounds are not detectable by XRF.
With the scientific progress achieved in the 19th century a number of new pigments were developed. Zinc white (ZnO) was used from the 19th century on and titanium white (TiO$_2$) became available in the 1920s. Next to a broad range of synthetic organic dyes and pigments, Prussian Blue (Fe$^{\text{III}}$[Fe$^{\text{II}}$(CN)$_6$]$^-$ with different cations), a wide range of yellow and orange chromates, chrome oxide greens and cadmium compounds ranging from yellow to red became available to artists, opening new ways of painting.

It is obvious that in many cases the knowledge of the elements present, in combination with the visual impression of the painting, are sufficient to identify the pigments present.

However, this is not always the case. Discrimination between malachite, green verditer and verdigris, based on XRF investigations alone is not possible. If no additional information is available, e.g. from the analysis of a sample taken from the painting or molecular spectroscopy, these pigments can just be identified as belonging to the group of “Cu containing green pigment”.

The presence of an anachronistic pigment allows to identify areas of restoration treatments. The degradation of pigments in historical paintings is a well known problem and is subject to a range of publications [35-43].
Table 1 Typical pigments used in easel paintings. Elements well detectable by XRF are printed in bold, while elements only weakly detectable are printed in italic.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Colour</th>
<th>Composition</th>
<th>Time period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead white</td>
<td>white</td>
<td>$2\text{PbCO}_3\cdot\text{Pb(OH)}_2$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Zinc white</td>
<td>white</td>
<td>$\text{ZnO}$</td>
<td>1920s-</td>
</tr>
<tr>
<td>Titanium white</td>
<td>white</td>
<td>$\text{TiO}_2$</td>
<td>-18th century-</td>
</tr>
<tr>
<td>Azurite</td>
<td>blue</td>
<td>$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$</td>
<td>15th century-</td>
</tr>
<tr>
<td>Blue verditer</td>
<td>blue</td>
<td>$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$</td>
<td>15th century-</td>
</tr>
<tr>
<td>Malachite</td>
<td>green</td>
<td>$\text{Cu}_2\text{CO}_3(\text{OH})_2$</td>
<td>-18th century-</td>
</tr>
<tr>
<td>Green verditer</td>
<td>green</td>
<td>$\text{Cu}_2\text{CO}_3(\text{OH})_2$</td>
<td>15th century-</td>
</tr>
<tr>
<td>Verdigris</td>
<td>green</td>
<td>$\text{Cu}$ corrosion products, mainly acetates</td>
<td></td>
</tr>
<tr>
<td>Emerald green</td>
<td>green</td>
<td>$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot3\text{Cu(AsO}_2)_2$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Vermilion/</td>
<td></td>
<td>$\text{HgS}$</td>
<td></td>
</tr>
<tr>
<td>Cinnabar</td>
<td>red</td>
<td>$\text{Pb}_3\text{O}_4$</td>
<td></td>
</tr>
<tr>
<td>Minium</td>
<td>red</td>
<td>$\text{Fe}$ oxides and hydroxides</td>
<td></td>
</tr>
<tr>
<td>Ochres</td>
<td>yellow</td>
<td>$\text{Fe}$ and $\text{Mn}$ oxides and hydroxides</td>
<td></td>
</tr>
<tr>
<td>Sienna</td>
<td>brown</td>
<td>$\text{Fe}$ and $\text{Mn}$ oxides and hydroxides</td>
<td></td>
</tr>
<tr>
<td>Umber</td>
<td>brown</td>
<td>$\text{SrCrO}_4$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Cadmium yellow</td>
<td>yellow</td>
<td>$\text{CdS}$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Cadmium red</td>
<td>red</td>
<td>$\text{CdSe}$</td>
<td>20th century-</td>
</tr>
<tr>
<td>Viridian green</td>
<td>green</td>
<td>$\text{Cr}_2\text{O}_3\cdot2\text{H}_2\text{O}$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Chrome oxide green</td>
<td>green</td>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Chrome yellow</td>
<td>yellow</td>
<td>$\text{PbCrO}_4$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Strontium chromate</td>
<td>yellow</td>
<td>$\text{SrCrO}_4$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Lead tin yellow</td>
<td>yellow</td>
<td>$\text{Pb}_2\text{SnO}_4$</td>
<td>15th -18th century</td>
</tr>
<tr>
<td>Naples yellow</td>
<td>yellow</td>
<td>$\text{Pb}_2\text{Sb}_2\text{O}_7$</td>
<td>17th century-</td>
</tr>
<tr>
<td>Prussian blue</td>
<td>blue</td>
<td>$\text{MFe}^{III}[\text{Fe}^{II}(\text{CN})_6]\cdot\text{nH}_2\text{O}$, with M being $\text{K}$, $\text{Na}$ or $\text{NH}_4^+$</td>
<td>18th century-</td>
</tr>
<tr>
<td>Smalt</td>
<td>blue</td>
<td>ground $\text{Co}$-rich glass, often containing $\text{K}$, $\text{Fe}$, $\text{Ni}$, $\text{As}$, $\text{Bi}$.</td>
<td>approx. 16th to 18th century</td>
</tr>
<tr>
<td>Ultramarine/Lapis Lazuli</td>
<td>blue</td>
<td>$\text{Na}_7\text{Al}_6\text{Si}<em>6\text{O}</em>{24}\text{S}_3$</td>
<td></td>
</tr>
<tr>
<td>Cobalt blue</td>
<td>blue</td>
<td>$\text{CoAl}_2\text{O}_4$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Cerulean blue</td>
<td>blue</td>
<td>$\text{CoO}\cdot\text{nSnO}_2$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Dark cobalt violet</td>
<td>purple</td>
<td>$\text{Co}_3(\text{PO}_4)_2$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Light cobalt violet</td>
<td>purple</td>
<td>$\text{Co}_3(\text{AsO}_4)_2$</td>
<td>19th century-</td>
</tr>
<tr>
<td>Bone/Ivory black</td>
<td>black</td>
<td>black carbon, $\text{CaPO}_4$, as remnant of the burned bones</td>
<td></td>
</tr>
</tbody>
</table>
1.1.3 Methods for the investigation of historical paintings

The methods discussed differ in form of contrast mechanism and the lateral dimensions of the results obtained. Next to one dimensional depth profiles (also called A-scans in analogy to ultrasonic imaging) and 2-dimensional virtual cross-sections (B-scans) also 3-dimensional data sets can be obtained. However, many techniques are limited to 2-dimensional projections of the 3 dimensional objects in that the depth information is subject to interpretation. If elemental or chemical contrast is employed, stacks of these data formats are obtained.

Measurements are done in transmission or reflection geometry. While the exact effect on the obtained information is dependent on the technique used, it can be said that in general measurements in reflection geometry are more sensitive to the surface. Further, reflection geometry measurements are easier to execute as the painting has to be accessed only from the front and contributions from support and mounting (e.g. the easel) are reduced or eliminated. From a practical point of view it is also easier to move radiation source and detector in front of the painting on the same motorized stage than to move them synchronized before and behind the painting. Motorized stages capable of moving a small painting are easily available, but precise motorized stages for large paintings, allowing for the movement of several tens of kilos, are expensive.

Most techniques discussed below scan the painting in one dimension with a flat beam, two dimensions with a focused beam or even three dimensions if a focused beam is combined with depth discrimination (s. Figure 2). A few techniques allow for the full field acquisition of a 2-dimensional projection, but all these techniques may require additional scanning in the spectral or time domain. If the resolution of an individual full-field image is limited it might be necessary to acquire images of various sub-parts of the painting that are afterwards assembled into a mosaic image.

The scientific techniques discussed are summarized in Table 2.

The oldest scientific technique for the investigation of easel paintings is X-ray radiography (XRR). It was first applied at the end of the 19th century within a year after discovery of the X-rays [44]. While considerable technical progress was made in terms of digitalization of detectors it is still applied in many restoration workshops with analogue films like decades ago. XRR is mainly used to study paint layers and support of paintings. In the recent years energy resolved X-ray radiography has been developed and extend the capabilities of XRR.
Infrared photography has been used in the investigation of historical paintings since the early 20th century. However, it was not until the 1960s that with Infrared Reflectography (IRR) a technique for the visualization of underdrawings was found [45, 46]. Similar to X-ray radiography, IRR is today an established technique and considerable progress has been made with the development of digital detectors and multispectral imaging in the IR range.

X-ray fluorescence spectrometry (XRF) has been used for the identification of pigments in paintings since many years [47], but it was not until recently that the value of elemental distribution images acquired by scanning macro-XRF (MA-XRF) for the visualization of sub-surface paint layers was demonstrated [48]. Since the first experiments at SR sources mobile instruments that allow for in-situ investigations have been developed.

Confocal XRF allows for the acquisition of depth profiles with elemental contrast [49]. It has made a development similar to MA-XRF from SR sources to instruments suitable for operation in museum workshops.

Optical coherence tomography (OCT) employs partly coherent light from the near infrared region to detect interfaces in completely or partly transparent materials. OCT found application in the medical field, so that mature instrumentation is available for the investigation of paintings [50, 51].

Unilateral NMR instrumentation is known since several years, but it was not until recently that it was applied to study organic binders in easel paintings [52].

The not exploited part of the electromagnetic spectrum called “Terahertz gap” has been closed in the last years due to progress in instrumentation and studies on the investigation of easel paintings and other cultural heritage artefacts have been described in the last years [53].

A number of techniques used in Non Destructive Testing (NDT) for industrial products have been successfully applied to investigate the conservation status of paintings. Laser based holographic methods [54] and thermography [55] were already proposed in the 1970s for the investigation of historical paintings, while ultrasonic imaging was described 20 years later [56].
## Table 2 Mobile sub-surface imaging and depth profiling techniques discussed.

<table>
<thead>
<tr>
<th>Method</th>
<th>acronym</th>
<th>Radiation</th>
<th>Contrast</th>
<th>Information</th>
<th>Geometry</th>
<th>scanning dimensions</th>
<th>lateral resolution</th>
<th>depth resolution</th>
<th>additional dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray radiography</td>
<td>XRR</td>
<td>X-rays</td>
<td>absorption</td>
<td>projection of electron transmission density</td>
<td>full field, 1 D</td>
<td>&gt;200 μm</td>
<td>n.a.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy dispersive X-ray radiography</td>
<td></td>
<td>X-rays</td>
<td>element specific absorption</td>
<td>projection of elemental distribution</td>
<td>full field, 1 D, 2 D</td>
<td>200 μm</td>
<td>n.a.</td>
<td>spectral</td>
<td></td>
</tr>
<tr>
<td>Scanning macro-XRF</td>
<td>MA-XRF</td>
<td>X-rays</td>
<td>distribution</td>
<td>projection of elemental distribution</td>
<td>reflection</td>
<td>2 D</td>
<td>50 μm</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Confocal XRF</td>
<td>cXRF</td>
<td>X-rays</td>
<td>element distribution</td>
<td>depth profiles of elemental distribution</td>
<td>reflection</td>
<td>1-3 D</td>
<td>50 μm</td>
<td>50 μm</td>
<td></td>
</tr>
<tr>
<td>Infrared Reflectography</td>
<td>IRR</td>
<td>Near Infrared</td>
<td>absorption</td>
<td>projection of total absorption</td>
<td>reflection</td>
<td>full field, 2 D</td>
<td>100 μm</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>Multispectral Imaging</td>
<td>Near Infrared</td>
<td>species specific absorption</td>
<td>projection of absorbing species</td>
<td>reflection</td>
<td>full field, 1 D, 2 D</td>
<td>&gt;500 μm</td>
<td>n.a.</td>
<td>spectral</td>
<td></td>
</tr>
<tr>
<td>Terahertz</td>
<td>THz</td>
<td>species specific absorption, scattering, reflection</td>
<td>3D data sets of interfaces and projections of absorbing species</td>
<td>transmission and reflection</td>
<td>2 D</td>
<td>300 μm</td>
<td>50 μm</td>
<td>time</td>
<td></td>
</tr>
<tr>
<td>Optical coherence tomography</td>
<td>OCT</td>
<td>Near Infrared</td>
<td>reflection, scattering</td>
<td>3D data sets of interfaces</td>
<td>reflection</td>
<td>1 D, 3 D</td>
<td>10-30 μm</td>
<td>1-10 μm</td>
<td></td>
</tr>
<tr>
<td>unilateral NMR</td>
<td>NMR</td>
<td>magnetic fields - 3H abundance and molecular mobility</td>
<td>depth profiles of 3H abundance</td>
<td>reflection</td>
<td>1 D</td>
<td>10 mm</td>
<td>10 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser interference techniques</td>
<td>optical</td>
<td>deformation under stress</td>
<td>projection of sub surface defects</td>
<td>reflection</td>
<td>full field</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Sound waves</td>
<td>propagation of sound waves</td>
<td>projection of sub surface defects</td>
<td>transmission and reflection</td>
<td>2 D scanning</td>
<td>n.a.</td>
<td>n.a.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermography</td>
<td>mid-IR</td>
<td>heat transport</td>
<td>projection of sub surface defects</td>
<td>transmission and reflection</td>
<td>full field</td>
<td>n.a.</td>
<td>n.a.</td>
<td>time</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2 a) Schematic of data dimensionality. b) Schematic scan dimensionality and measurement geometries. S=Radiation Source, D=Detector
1.2 X-ray based methods

1.2.1 Radiography and related techniques
XRR was the first technique that allowed one to obtain information about sub-surface structures in historical paintings in a non-destructive manner [44]. Today it is an established technique for the investigation of historical paintings. It is practiced in many conservation studios and is suitable for screening large numbers of paintings, as a single radiograph can be taken in a matter of minutes [57].

XRR is a transmission technique in that absorbance of X-rays in a painting is imaged. Commonly full-field detection is employed, but also one dimensional scanning systems employing fan beams and line detectors are used, as well as two dimensional scanners employing pencil beams were described [58]. To record the transmitted radiation in full-field either films or digital detectors are used. Xeroradiography (“dry radiography”) in that the radiograph is directly recorded on paper has fallen into disuse with the rise of digital radiography, but its application in the investigation of easel paintings is described in [59].

The main advantage of analogue films is the higher lateral resolution obtained with them. This is due to the fact that the grain size in X-ray films is in the range of 2 micrometers, while the pixel size of commercial digital detectors is several tens of micrometers. However, analogue film radiography requires more time and results in a higher dose of radiation absorbed by the investigated object compared to digital radiography as the limited sensitivity of films requires longer exposures. The limited dynamic range of films requires often test exposures to determine the best voltage, current and exposure time combination. Digital radiography requires no time consuming processing of films and directly provides digital data for advanced image processing [60].

In the medical field, where radiation dose and speed are crucial and a slightly inferior resolution is acceptable if an good contrast is obtained, digital radiography replaced film radiography [61]. In the investigation of cultural heritage these are less pressing issues and given the costs of acquiring new systems, digital radiography has been only slowly replacing analogue film radiography.

No information on the elements present is obtained in XRR. It is, for example, not possible to distinguish in a radiograph between paint layers with a high abundance of heavy elements (Pb, Hg) or thicker layers with moderately strong absorbing elements (Zn).
Since absorption follows the Beer-Lambert law, the contrast obtained is not only dependent on the absorption power of a given paint layer, but also the absorption power of layers above or below it in the paint stratigraphy. Thin paint layers that are themselves applied to a weakly absorbing support would be clearly reproduced by XRR. However, if they were painted on a thick lead white ground they would not be discernible. This can be observed in Figure 3, showing a part of the radiograph of Saul and David by Rembrandt van Rijn and/or his workshop from the collection of the Mauritshuis Museum in Den Haag. At an unknown moment in the past the painting has been cut-apart and re-assembled, resulting in the visible joints. As can be seen in the elemental distribution images acquired by MA-XRF the face of David is executed in earth pigments (Fe) and probably bone black (Ca) with only a few accents set with lead white (Pb). These paint layers are considerably less strongly absorbing than the lead white containing ground, so that in the radiograph the contribution of the paint layers is barely discernible. The results shown were obtained during the investigation performed for [62].

In Figure 4 Flower Still Life with Meadow Flowers and Roses by Vincent van Gogh is shown. As discussed in Chapter 4 and [63, 64] the flower still life was executed on a wrestling scene created by Van Gogh approximately half a year earlier. Although the main white pigment in the flower still life is lead white and the wrestlers were mainly executed in zinc white a clear reproduction of the wrestlers is achieved, except in areas where thickly painted flowers dominate the radiograph. This is due to the fact that the zinc white layers in the wrestlers were so thickly painted (in parts more than 500 µm) that they are clearly discernible next to the thinner lead white layers.

The contributions of support and ground layers can make the radiographs difficult to read, so that different approaches were taken to reduce their influence. Next to the removal of cradle (panel paintings) or stretcher (canvas paintings) from radiographs by digital post processing, filling the interstices of the cradle members with sugar, a material with X-ray absorption characteristics similar to wood, has been described [65]. Another method is strati-radiography, in that the film is placed directly on the painting and the X-ray tube is moved during the exposure, resulting in a blurring of the support in the obtained radiograph [1]. In stereo-Radiography two X-ray radiographs taken with different X-ray tube positions are combined to a stereographic image, which is especially helpful for the investigation of panels that were painted on both sides [1].

The contribution from the panel support can be nearly eliminated by employing electron emission radiography [66]. Here the film is placed
directly on the paint layers. Both are exposed to the X-rays, which pass through the film before reaching the painting. The X-ray tube is operated at a high voltage (several hundred kV) with a suitable filter absorbing the lower energetic part of the tube spectrum. The photoelectrons emitted by the surface layers of the painting darken the film, while the high energy X-rays pass through it without interaction. The method is also suitable for the investigation of paintings on Cu plates in which the paint layers are not discernible in conventional radiographs [67]. Given the strong absorbance of electrons in paint layers the images obtained are dominated by surface paint layers with covered layers making only minor contribution. Electron emission radiography has also been subject to a recent comparison of radiography techniques [68].

On the other hand XRR also allows for a study of the support of paintings. If a canvas painting is lined its original canvas can no longer be directly investigated. As the ground layer of a painting follows the weave pattern of the canvas and is stronger absorbing X-rays than original and added canvas, the weave pattern can be (indirectly) discerned in the radiograph. Recently a computer algorithm was presented that detects thread density variations in these weave pattern. These variations can be read as a fingerprint of the loom the canvas was made on. Paintings made on canvas from the same loom can so be identified. Further, this form of data processing enhances the visibility of cusings [69, 70]. The algorithm was applied on the radiographs of more than 380 paintings by Vincent van Gogh and produced additional arguments for their order of creation [71]. Comparable results were obtained in a similar study on a number of paintings by Johannes Vermeer [72].

XRR was also found useful to study the wooden support of panel paintings [73, 74]. Computed tomography (CT) gives additional information on the wooden panels, as it allows for the acquisition of three dimensional data sets reconstructed from a series of X-ray radiographs [75-77]. CT data allows to visualize wormholes, cracks and other features of the internal structure of panel paintings. Mobile CT instruments designed for in-situ investigation of large cultural heritage artefacts have also been described [78]. CT can be employed to register the year ring pattern of wooden blocks for dendrochronological dating [79], but has to my best knowledge not been successfully applied to the support of an panel painting due to the limited lateral resolution. Paintings do not constitute optimal samples for investigation by CT, as laterally extended objects are rather problematic due to strong absorption in the directions parallel to the lateral elongation. So it is not possible to resolve individual paint layers. An alternative to this might be computed laminography (CL). The technique is similar to CT, but a
measurement along the lateral elongation is avoided by rotating the sample around an axis that is tilted relative to the radiation source-detector axis [80]. CL has been used to investigate a test painting sample at SR sources. The spatial resolution of 7.5 µm was found sufficient to distinguish between paint and grounds layers(s) [81]. However, no application on cultural heritage with an X-ray tube source has yet been described.

Figure 3 Rembrandt and/or Studio, Saul and David, c.1655, Mauritshuis, The Hague (NL), inv. no. 621 / Bredius, no. 526, oil on canvas, 126 x 158 cm (original canvas); 130.5 x 164.5 cm (stretcher). The pictorial layers used to model the face of David are not discernible in the XRR. For comparison results obtained by MA-XRF are shown. These reveal that these elements of the painting were executed in earth pigments (Fe) and bone black (Ca) with minor additions of lead white (Pb), which are in total much less absorbing than the lead white ground. The results shown were obtained in the framework of the experiments described in [62].

1.2.2 Energy resolved radiography
While XRR is an established and reliable imaging technique, radiographs are dominated by the strongest absorbing layer and only few conclusions on the elements present can be drawn, since in conventional detectors only the number of photons is registered, not their energy. Energy resolved radiography can considerably enhance the contrast of radiographs and potentially image elemental distributions. Like conventional XRR, energy resolved XRR is a transmission technique.

In dichromography or K-edge imaging energy resolution is achieved by employing primary radiation of different energies. Commonly, flat beams of the selected energy are obtained by Bragg diffraction on a monochromator, necessitating one dimensional scanning of the painting.

By subtracting images acquired with energies above and below the absorption edge of an element its distribution image can be obtained. The
technique was first in detail described by Jacobson and is long applied in the medical field [82, 83]. Yet, it took several decades before the technique was applied on paintings [84]. Recently a dedicated X-ray source, emitting a monochromatic fan beam, was described [85]. Other groups used K-edge imaging at SR sources [68, 86].

Results published for K-edge imaging of historical painting are mostly limited to proofs of principle on test samples, with the exception of [85] in which the Zn distribution in a modern painting is shown. While the X-ray tube based instruments are too large to be easily transported into a gallery, an installation in a laboratory is possible and was realized in the Italian neu_ART project. This laboratory also contains facilities for conventional radiography of large paintings and X-ray tomography [77].

Energy resolved radiography can also be achieved by energy dispersive detection. Zemlicka et al. [87] employed a Timepix detector for the construction of a mobile instrument that allowed for data acquisition without lateral scanning. The Timepix is a hybrid semiconductor pixelated detector that allows for the energy dispersive detection of individual X-ray photons. Their instrument proved capable of separating support and paint layers in the energy dispersive radiography of a mock-up of a 19th century painting.

Schalm et al. compared different radiographic techniques in an attempt to enhance the contrast obtained [68]. Next to electron emission radiography (see above) and dichromatic radiography at SR sources, an experimental set-up for energy resolved radiography was described. The set-up consists of a W-anode X-ray tube source and a collimated, energy dispersive silicon drift detector without lateral resolution. For the acquisition of images two dimensional lateral scans are required. While the instrument is not meant for routine applications it allowed to illustrate the possibilities of energy dispersive radiography and provided radiographs with reduced contributions from ground layers and support.

From the same research group Cabal et al. [88] employed the same experimental set-up for elemental imaging via K-edge subtraction and contrast enhancement by Principal Component Analysis (PCA). Their general conclusion, which is in good agreement with the results presented by other groups, is that elements with an absorption edge significantly below 10 keV can only be imaged if only low amounts of stronger absorbing, heavier elements are present. Heavier elements, such as Hg (Hg-L3 edge: 12.3 keV) or Cd (Cd-K edge: 26.7 keV) can still be imaged if lead white was employed as a white pigment. Until now, energy dispersive radiography did not find wide application in the investigation of paintings, but might benefit from progress in detector development.
1.2.3 Scanning macro-XRF
The fluorescence radiation emitted from a sample that is exposed to an X-ray beam contains qualitative and quantitative information about the elements present. Elemental distribution images are commonly acquired by two dimensional scans with a focused or collimated primary beam in reflection geometry. Given the penetrative nature of X-rays, fluorescence radiation is not only recorded from the surface paint layers, but also from covered layers and at times the ground layers. Scanning micro-XRF (mXRF) with a resolution in the micrometer range is an long established technique in the investigation of cultural heritage objects, but the construction of scanners for macroscopic objects is technically challenging [89]. Since the beginning of the 1990s several instruments have been described and their value demonstrated in case studies [90-94]. Also a commercially available system, the Artax (Röntec GmbH, Berlin, now Bruker Nano GmbH, Berlin, Germany) was presented and used in case studies [95, 96]. However, all of these scanners typically required several seconds of dwell time per pixel, limiting their application to small details; e.g. a scan of 5x5 cm with a resolution of 1 mm and a dwell time of 5 seconds would ask for more than three hours.

Given the lack of suitable mobile instrumentation Vincent van Gogh’s Paris period painting *Patch of Grass* was investigated at the Deutsches Elektronen Synchrotron (DESY, Hamburg, Germany) in 2007 by Dik et al.. By employing a collimated monochromatic beam they visualized a discarded and overpainted study of a peasant’s head, hidden underneath the later painting [48]. This experiment was followed by several other case studies at DESY. An overpainted composition under *The laughing Rembrandt* by Rembrandt van Rijn was studied in 2009 [97]. Large *pentimenti* in hairstyle and facial expression could be visualized in *Pauline im weißen Kleid*, a 19\textsuperscript{th} century painting attributed to Philipp Otto Runge [98]. In a study of the hidden painting under Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* convincing arguments for his, until then generally doubted, authorship could be found (s. Figure 4, Chapter 3 and [63, 64]). At the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory, NY, USA) the underpainting under Rembrandt’s *Portrait of an Old Man* could be visualized and was crucial in confirming his authorship [99]. At the Australian Synchrotron (Melbourne, Australia) an discarded and overpainted self-portrait by Arthur Streeton could be reconstructed by means of XRF imaging [100].

Even though these experiments gave new and important insights, it is obvious that only a small number of paintings can be transported to SR sources. Given that pigments are commonly present at a concentration level
of several mass percent it is to be expected that a well designed mobile scanner would be capable of visualizing the main constituents of a painting with a dwell time of (fractions of) a second. Such a device, making use of four detectors to record fluorescence radiation from a large solid angle and X-ray sources of 10 or 50 W for excitation was developed in this work [64, 101]. A high sensitivity is achieved by positioning the measuring head approximately 1 cm away from the painting in order to a) avoid the absorption of low energetic fluorescence lines in the air and b) to enlarge the solid angle from that the fluorescence radiation is recorded, as it depends on the inverse squared distance to the surface. Due to the acceptance of MA-XRF among art-historians and conservators Bruker nano GmbH (Berlin, Germany) developed a commercially available scanner labelled “M6 Jetstream” [102]. The development of these scanners is discussed in Chapter 2.

In these scanners lateral resolutions below 100 µm can be achieved, but cannot be exploited for large areas, given the nature of MA-XRF as a scanning technique with two lateral dimensions. To scan an area of 50x50 cm with a lateral resolution of 100 µm and a dwell time of 20 ms per pixel six days would be necessary. However, with a lateral resolution of 500 µm the same area can be investigated in just more than 5 hours.

The value of the mobile scanner was also shown in a number of case studies. The mobile scanner was used to complement the results obtained on Vincent van Gogh’s Flower Still Life with Meadow Flowers and Roses at the synchrotron [63, 64]. This study also demonstrated that mobile instruments can achieve a sensitivity comparable to SR based scanners for elements with characteristic fluorescence radiation below 15 keV. Saul and David by Rembrandt and/or his studio was investigated in order to reveal the extent of original paint still present before a conservation treatment [62]. MA-XRF investigations of Goya’s Portrait of Don Ramón Satué revealed details of an underlying portrait that allowed to identify the sitter as an Spanish officer serving during the reign of king Joseph Bonaparte [103]. Two versions of Caravaggio St. Francis in Meditation were investigated to detect pentimenti and compare the pigment use with autograph paintings [104]. Further, a full scale mock-up of Rembrandt’s Old Man in Military Costume from the collection of the Getty Museum (CA, USA) was used to compare the imaging capabilities of an (early) mobile scanner and two SR based scanners [105].

The case studies on Rembrandt and/or studio’s Saul and David, Rembrandt’s Portrait of an Old Man, Goya’s Portrait of Don Ramón Satué, Caravaggio’s St. Francis in Meditation, Pauline im weißen Kleid and Vincent van Gogh’s
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*Flower Still Life with Meadow Flowers and Roses* are discussed in more detail in Chapter 4.

MA-XRF investigations reveal the distribution of elements in surface and sub-surface layers, allowing in many cases the identification of pigments used. XRF is a highly developed form of spectrometry in that, in case of a skilled operator and a well designed system, all spectral features can be identified and a false positive identification of an element is highly unlikely. However, as discussed above, discrimination between different pigments with identical elemental markers is not directly possible.

A limitation of MA-XRF is that the characteristic fluorescence radiation investigated with mobile scanners is of low energy (less than 30 keV) and so absorbed in the painting. Due to the reflection geometry the acquired elemental distribution images are dominated by the surface layers and light elements in hidden layers might not be observable. In Figure 5 the calculated thickness of a lead white layer (80 mass% lead white, 20 mass% alpha-linolenic acid as organic medium) absorbing 90% of the emitted fluorescence radiation of an element is shown. As most paint layers contain many components considerably less absorbing than Pb many elements can be observed (attenuated) through paint layers a multiple of the thickness, but as in radiography the contrast to other layers determines the readability of the images.

In Figure 4 elemental distribution images obtained on Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* are shown. As discussed above the flower still life was executed directly on an older wrestling scene. Preliminary investigations revealed that the flower still life is too absorbent to visualize the hidden wrestlers by measuring through it. So, the painting was during the experiments at DESY positioned with its canvas to the beam and detectors on both sides of the painting. The main interest was the visualization of the Zn distribution, as this element was used to execute the flesh tones of the wrestlers. The data recorded from the back side of the painting contained considerable absorption artefacts from ground, canvas and glue layers, but, given the homogeneous nature of these absorbers and their known stratigraphy, the distribution image could be corrected (see [64] and Chapter 3 for details). Also in the Zn distribution image recorded by the front detectors considerable absorption artefacts can be observed, which make the shape of the wrestlers hardly discernible. Also a clear discrimination between Zn present in covered layers and Zn at the surface is not possible. An absorption correction, as in case of the detectors positioned on the back side, is not possible, given the far more complex unknown stratigraphy of the absorbers.
Also elements beyond Zn are detectable in the painting. Hg is detectable from both sides of the canvas, but the distribution image recorded by the front detector only reveals the usage of vermilion in the flower still life. The back side detectors allow to discern highlights set to the flesh tones of the wrestlers, but also contains contributions of the thickly painted red flowers. The detectors on both sides yield comparable results for Ba, as it is due to its high fluorescence energy (32.2 keV) only weakly absorbed. The Pb distribution of the pictorial layers can only be visualized from the front detector, as behind the original canvas a thin lead white layer is present, which dominates the obtained distribution image. These results were obtained at the DESY synchrotron and not with a mobile instrument. However, as the DESY synchrotron scanner and the latest mobile scanner feature for the elements discussed, with the exception of Ba, a comparable sensitivity, these results could have also been obtained in-situ [64].

While these absorption effects can complicate the interpretation of elemental distribution images they contain information about the stratigraphy of a painting [19]. This was successfully demonstrated on several painting from collection of the Louvre (Paris, FR). In these studies the thickness of paint layers and covering glaze layers was calculated [106, 107]. Further, advanced data processing routines have been applied in order to remove absorption artefacts from elemental distribution images and reconstruct overpainted artworks [108]. Depth discrimination in case of MA-XRF investigations is discussed in Chapter 3.
Figure 4 Vincent van Gogh, *Flower Still Life with Meadow Flowers and Roses*, summer 1886 (Kröller–Müller Museum, Otterlo, the Netherlands. Oil on canvas, 100×80 cm, KM 100.067, FH 278, JH 1103) as photograph and X-ray radiograph. Elemental distribution images were acquired by MA-XRF simultaneously from both sides at DESY, Hamburg (DE) and illustrate the effect of absorption in covering layers on the readability of elemental distribution images.
The main limitations of MA-XRF are the slow data acquisition as a scanning technique and the lack of species information. Recently developed energy dispersive cameras make full-field XRF imaging feasible [109]. However, also the camera described in aforementioned reference is limited to the investigation of small areas (a few square centimetres) and is not capable of taking overview images of the whole surface of an average painting (50x50 cm) in a single exposure. The intensity of the fluorescence lines compared to that of the primary and transmitted radiation is low and for reasons discussed above the camera must be positioned close to the painting’s surface to enhance its sensitivity. An instrument that stitches a mosaic of different small XRF maps acquired with such a camera might be feasible.

Zemlicka et al. employed their Timepix detector as an energy dispersive camera for Full-Field XRF on a replica of a 19th century painting and obtained elemental distribution images of Cd and Se. The Timepix detector was not designed as a fluorescence detector and features an energy resolution of approximately 3 keV, so that an identification of elements in a complex matrix such as a painting can be considered challenging.

1.2.4 Scanning XRD

X-ray diffraction (XRD) is a technique routinely employed for the in-situ identification of cultural heritage objects [110]. It complements investigations by XRF, as it allows the identification of different phases. It is,
e.g., not possible to distinguish between goethite ($\alpha$-FeO(OH)) and hematite ($\alpha$-Fe$_2$O$_3$) via XRF investigations, but by XRD.

The application of XRD in the investigation of large samples is commonly limited to point measurements, but at SR sources XRD has been employed for scanning experiments on cultural heritage objects. Dooryhée et al. investigated fragments of a wall paintings in reflection geometry [111], while De Nolf et al. used an 86 keV primary beam to demonstrate the imaging capabilities of XRD in transmission geometry for covered layers in panel paintings [112]. The fact that primary and secondary radiation have in XRD experiments the same energy also reduces the absorption effects that prevent the visualization of light elements in covered paint layers by XRF. Scanning XRD imaging is slow, asking for dwell times of more than one second per pixel, even when employing high intensity SR beams. To penetrate paint layers and support of a painting, monochromatic beams of high energy need to be employed. As monochromatic beams above 25 keV are commonly not available from X-ray tubes suitable for mobile scanners, scanning XRD might be often limited to reflection geometry. Nevertheless, XRD allows for the identification of crystalline phases in hidden layers that cannot be identified by other methods and at times not even detected, so that a mobile XRD scanner for (small sub-areas) of paintings would allow to obtain information complimentary to MA-XRF.

1.2.5 Confocal XRF

In conventional micro-XRF the focused primary beam can penetrate several layers of the sample and all contribute to the acquired XRF spectrum. In confocal-XRF the field of view of the detector is restricted by the insertion of a polycapillary half lens and at the intersection of the two optics’ foci the information volume is formed from which XRF radiation is recorded. The lateral distribution of elements is determined by moving the sample through the information volume. The investigation of cultural heritage artefacts by confocal XRF has been subject to an recent review article by B. Kanngießer [3].

Confocal XRF has been applied for the investigation of historical paintings at SR sources in order to obtain 1-dimensional depth profiles [49], 2-dimensional virtual cross-sections [113] or even 3-dimensional data cubes [114]. Confocal instruments at SR sources commonly achieve a depths resolution of 10 µm and require dwell times of a few seconds or less. X-ray tube based instruments were reported briefly after the first synchrotron experiments and can achieve a depth resolution in the order of 40 µm, but the inferior sensitivity necessitates dwell times of several tens of seconds per pixel [115, 116]. One has to be aware of the chromatic aberration of
polycapillary lenses, as it causes an energy dependent depth resolution that decreases with higher energies. Due to the energy dependent efficiency of polycapillary lenses, confocal XRF with X-ray tube sources is in the investigation of historical paintings best suited for the detection of elements between K (Z=19) and Zr (Z=40) by their K-shell and heavier elements by their L-shell fluorescence radiation.

Reiche et al. investigated two Renaissance paintings with a X-ray tube based confocal instrument in the laboratory of the Louvre (Paris, FR) and compared the results with cross sections taken near the analyzed spots [117]. Both paintings belong to the series Famous Men completed in 1475/1476 for Federico da Montefeltro. They were capable of achieving results comparable to paint cross section and confirm suspected later modifications to the paintings.

Confocal XRF has several limitations. The dwell time of several tens of seconds necessitates long scans (approximately half an hour) for a single depth profile, making the acquisition of virtual cross sections and 3D data sets feasible but very time consuming. Further, since only a small area is investigated, great care needs to be taken in order to select a representative spot for analysis. Absorption in covering paint layers is limiting this technique typically to less than the first 200 µm (depending on fluorescence energy of the investigated element and composition of absorbing layers). Finally, paint layers can be of less than 10 µm thickness, considerably smaller than the depth resolution. So care must be taken to not miss such a layer in data evaluation if it is above or below a layer with similar composition. However, confocal XRF constitutes the only non-destructive depth profiling method with elemental contrast that can be applied in conservation studios and is expected to find in the future application in combination with other imaging techniques. Examples of cXRF measurements can be found in Chapter 3.
1.3 Infrared based methods

Infrared radiation is commonly associated with heat radiation and occupies in the electromagnetic spectrum the region between visible light and Terahertz radiation. The IR region can be divided in several regions, but the exact borders differ between publications. In what follows the borders set in [118] for the spectral region employed will be used: visible (VIS, 0.4-0.7 µm); near-infrared (NIR, 0.7-1.0 µm); short-wave infrared (SWIR, 1.0-2.5 µm) and mid-infrared (MWIR, 2.5-15 µm).

For the investigation of sub-surface layers of historical paintings by infrared reflectography (IRR) mainly a NIR and SWIR are used, as in this region the transparency of many pigments rises with the wavelength, while carbon-based black is still strongly absorbing. Higher wavelengths are not well suited as between 2.7 and 3.5 µm organic binders are strongly absorbing due to O-H and C-H vibrational bands. Longer wavelengths in the MWIR have been explored for IRR and are used in thermography (see below).

IRR is, like X-ray radiography, today an established technique for the in-situ investigation of historical paintings. However, IRR measurements are easier to perform as the radiation employed is conveniently available from conventional incandescent lamps and electronic flash tubes and constitutes no health hazards. As in XRR main developments in the recent years are the availability of digital detectors and the expansion into multi-spectral imaging.

1.3.1 Infrared photography and reflectography

The first application of IR radiation in the investigation of historical paintings was IR-photography, a simple, reflection geometry, full-field technique in that films sensitive to IR from 0.7-0.9 µm are used to record the radiation reflected by the painting. IR-photography offers the advantages of being easily applicable and showing the painting at a different contrast than XRR and observations under visible or UV light. It eases the identification of retouches, as pigment mixtures having the same colour in the visible range often have different absorption characteristics in the IR. Its disadvantage is that IR film is only sensitive up to a wavelength of 0.9 µm, so that sub-surface layers, such as underdrawings, can only be observed under a few pigments transparent at these wavelengths, e.g. ultramarine [1, 18]. With the technological progress of digital detectors IR-photography has fallen into disuse and replaced by Si CCD or CMOS cameras sensitive from 0.7 to 1.1 µm owing to their improved performance and availability [119, 120]. Falco recently described in great detail the modification of a commercial 8 Mpixel digital camera for IRR and discussed results obtained on a painting by
Lorenzo Lotto [121]. However, his interpretation of his findings was strongly criticized [122].

SWIR between 1 and 2.4 µm is much better suited for the observation of underdrawings as the transparency of most components in surface layers of paintings peaks in this region, while carbon-based black pigments are strongly absorbing. In order to exploit this spectral window J.R.J. van Asperen de Boer devised IR-Reflectography by replacing the film recording the IR radiation first with an IR camera [45, 123] and later a vidicon tube with an PbS target sensitive up to 1.9 µm [46, 124]. The term IR-Reflectography was chosen for a clear distinction to IR-Photography, as IRR allows a better observation of underdrawings at an inferior lateral resolution, due to the vidicon tubes employed.

Underdrawings can be best visualized in paintings dating to the 16th century and before. These paintings typically feature a strongly reflecting white ground with underdrawings executed in strongly IR absorbing carbon-based black pigments. In later centuries less IR-reflecting coloured grounds were used and the composition was sketched with white chalk, iron gall ink or underpainted with oil pigments. These materials are themselves largely transparent to the wavelengths employed in IRR, so that only a low contrast to the surface paint layers is obtained. Also strongly IR absorbing carbon-based black pigments present in the paint layers commonly prevent the observation of underdrawings. An example of an IRR investigation revealing underdrawing is shown in Figure 6, which shows minor modifications to the initial concept drawn.

The analogue vidicon tubes employed as detectors in IRR can only record a few hundred lines per image, introduce geometrical distortions and do not feature the same photometric response over their whole surface. In order to acquire high resolution IRR images of large paintings several reflectograms need to be stitched together, necessitating considerable overlap between the reflectograms as only their centre is free of geometrical distortions. High quality mosaic images ask for the high effort to record the detail reflectograms in identical geometry with identical illumination [125].

Several approaches were made in order to enhance the readability of reflectograms by improving spatial resolution and contrast and making the creation of mosaics easier or eliminate the need for it.

Instead of full-field acquisition reflectograms can be acquired by scanning. In 1990 Bertani described an IRR scanner achieving a spatial resolution of 0.2 mm in the spectral region between 1.1 and 1.5 µm [126]. Recently, Daffara et al. reported on an advanced scanner which records 14 bands in
the NIR and SWIR from 0.7 to 2.3 µm and allows for multispectral imaging, achieving a spatial resolution of 0.5 mm [127]. As scanning systems these instruments require measurement times in the range of hours to scan 1 square meter at maximum resolution.

Vidicons were replaced by solid state array cameras, which are easier to operate and free of geometrical distortions. The first material used was PtSi (sensitive to 1.0-5.0 µm), which required cooling by liquid nitrogen. In this system the spectral range acquired was adjusted by IR filters, which allows to select the spectral band best suited for the underdrawing material employed [119, 128, 129].

Today the most common material of solid state arrays for IRR is InGaAs. These detectors are sensitive to radiation between 0.9 and 1.7 µm, require no liquid nitrogen cooling and feature a higher quantum efficiency than vidicon tubes and PtSi solid state arrays. For the recording of longer wavelengths also solid state detectors made of HgCdTe and InSb are available, but these devices are considerably more expensive and also require cooling in order to obtain acceptable signal-to-noise ratios [6, 18, 130]. However, also the solid state detectors commonly available have a size of considerably less than 1 Mpixel, so that the stitching of sub-areas into a mosaic image cannot be avoided.

Saunders et al. devised a camera system that allowed to acquire 25 Mpixel IRRs with a lateral resolution of 10 µm. This is achieved by moving a small (320x256 pixel) InGaAs sensor on a motorized stage across the focal plane inside the camera. By exploiting the fact that the geometry inside the camera is reproducible a seamless stitching of the individual exposures becomes possible [130]. Their camera is lightweight and can easily be transported for in-situ measurements. A similar system is commercially available in form of the OSIRSI camera [131]. A camera operating in a similar manner was described in [132].

Dietz et al. described a 3D laser scanner operating at a wavelength of 0.785 µm, thus barely in the IR range, that not only records the intensity of the reflected beam but also acquires a topographic map of the paintings surface. While the current system is not capable of penetrating deeply into the painting and revealing underdrawings it might be a model for laser scanner of higher wavelengths [133].
Figure 6 Christ among the Doctors, oil on panel, 54.9 x 33.3 cm, Bernard van Orley, c.1513, (K-1669) Kress Collection, National Gallery of Art, Project of the National Gallery of Art and George Washington University. Photograph (left) and IRR acquired with a InSb camera equipped with a 2050 to 2400 nm spectral band pass filter, and spatial resolution of 290 dpi at the painting’s surface. Few modifications to the Christ are discernible, except that he has been sketched sitting on a podium. The background (building and people) has been only roughly sketched and modified later on. Most striking are the modification of the columns at the exit of the buildings, which have been sketched with considerably more decorations. (Copyright 2012 Samuel H. Kress Foundation)

1.3.2 Variants of Infrared reflectography

1.3.2.1 Infrared Luminescence
A small number of pigments emit IR radiation if exposed to green and blue visible light, allowing to obtain complimentary information to other imaging techniques. IR luminescence imaging has been proposed for the study of historical paintings in the 1960s [134]. It was used to study Egyptian blue, Han blue and Han purple on archaeological objects [135, 136], and
cadmium based pigments [137]. The later employed multi-spectral IR imaging to discriminate between different cadmium components. However, due to the limited transparency of paint layers to the primary radiation the method is not suited for the study of hidden paint layers.

### 1.3.2.2 Transmission

Measurements of canvas paintings in transmission geometry, which exploits their slight transparency to IR radiation, have been described several decades ago [138, 139]. Until recently the application of the method was hindered by the low sensitivity of IR detectors, which necessitated long exposure times. However, transmission IR images are less surface sensitive than reflectograms, so that underdrawings, not or only weakly visible in the IRR, can be observed in the transmission image. While care has to be taken to avoid stray light being detected in the camera, IR transmission images can be obtained with little effort if the equipment for IRR is available and can provide complimentary information to IRR and XRR [140, 141].

### 1.3.2.3 Higher wavelengths

Early studies in IRR employing next to the SWIR also the MIR band (1 to 5 µm) revealed that the optimal range for the visualization of underdrawing is 1 to ~2.5 µm, depending on the pigments and ground present [128, 129]. IRR with higher wavelengths features an overall lower contrast, but can provide complimentary information, as the absorption and reflection characteristic of many pigments is different in SWIR and MIR. Vermilion (HgS), for example, is strongly reflecting in the MIR, as opposed to the SWIR.

While up to 5 µm reflected radiation is more intense than the thermal radiation emitted by a body higher wavelengths are less well suited for IRR, as images acquired in this region are always a combination of thermograms and reflectograms. The MIR range has been recently exploited in the investigation of several frescos [142, 143].

### 1.3.2.4 Spectral imaging

Spectral imaging has been recently reviewed in [6, 118]. In this method stacks of 2-dimensional projections with identical spatial information are recorded at different wavelengths. The wavelength sensitivity is commonly achieved by employing narrow band filters in front of the camera in full field acquisition [144] or by scanning the surface with tightly assembled set of detectors [127]. While the first approach is susceptible to mechanical stability problems and chromatic aberrations the second approach is time consuming. Next to allowing for the selection of the wavelength providing best contrast for the underdrawing pigment and ground combination,
spectral imaging allows for the identification of pigments in surface layers [145, 146].

Delaney et al. used two hyperspectral cameras to acquire in total 260 bands from the visible (417 nm) to the Near-IR (1650 nm) range. Their cameras utilize slit based, scanning sensors, recording the image line by line with full spectral resolution. The system allows for the acquisition of 1 MPixel images in 4 minutes per camera. The increased spectral resolution of this system allowed for increased visibility of compositional changes in Blue Period Picasso paintings. Advanced data processing of the acquired spectral data allowed to separate and map the major pigments and identify most using spectral databases in combination with complimentary methods, such as XRF spot analysis [145, 147].

Daffara et al. used their scanner for the investigation of various Italian masterpieces, among them paintings by Caravaggio and Raphael. They demonstrated how the contrast observed in an IR reflectogram can be enhanced by selecting an adequate bandwidth and image manipulation operations, such as subtraction, ratio calculation and colour mixing [127, 148].
1.4 Optical coherence tomography

Optical coherence tomography (OCT) is a scanning, reflection geometry technique allowing for the investigation of objects moderately absorbing or scattering the probing light. OCT employs partly coherent, polychromatic light from near infrared region (0.7-1.5 µm) that is analyzed in an interferometer after being reflected by the painting. As the interfaces between layers with different absorption/scattering characteristics reflect the light back to the interferometer, OCT allows for the acquisition of depth profiles, virtual cross sections and (small) 3-dimensional data sets.

By taking the median of slices from a volume acquired by OCT with near-IR illumination, information complimentary to IRR can be acquired (see Figure 7) [149, 150]. These images feature a higher resolution and dynamic range as scattering and/or refraction in covering paint layers is eliminated. Further, this allows to discriminate covered layers from surface layers by selecting adequate slices. However, such investigations ask considerable more time than IRR measurements and are limited to small areas (a few square centimetres).

![Figure 7 After Francesco Francia, The Virgin and Child with an Angel, second half of the nineteenth century, detail of the eye of the angel (National Gallery, NG3937): a) colour image, © National Gallery London; b) 880nm CCD image; c) 900-1700nm NIR InGaAS image; d) 930nm OCT image (median of 40 en face images). Reproduced from [149] with permission.](image)

OCT commonly features a lateral resolution of 10 to 30 µm and a depth resolution of 1 to 10 µm. Scanning speed and maximum imaging depth vary considerably with different excitation and detector configurations, but in general a virtual cross-section can be acquired in a few seconds. OCT has been recently reviewed in detail by P. Targowski, also discussing more advanced full-field instruments [8, 9].
OCT gives a detailed insight in layering of the varnish layers and the topography of varnish and paint surface. However, by exploiting the fact that thin layers of many pigments are at least partly translucent for the light employed, OCT allows the study of thin paint layers close to the surface.

Depth-profiles, being acquired non-invasive, can be taken of larger areas than paint cross-sections and of areas too crucial to the painting to permit sampling. Further, embedding and polishing can cause cracks and delaminations in physical cross section obtained by sampling. In a virtual cross section acquired by OCT these artefacts can be excluded [151]. By means of OCT Targowski et al. found strong evidence of forgery of a signature in *Portrait of an unknown woman* created in the late 19th century by an unknown artist (s. Figure 8) [152].

![Figure 8 Virtual cross section through the signature of Portrait of an unknown woman. Two varnish layers, of which the lower, older one was mostly removed by cleaning, are positioned above the paint layer. Only in the area of the signature (red arrows) the paint surface is directly under the later varnish, suggesting its application after the first cleaning of the painting. It is worth noting that the original paint is still weakly discernible under the added signature. Reprinted with permission from [152]. Copyright (2013) American Chemical Society.](image)
1.5 Terahertz

Terahertz radiation is located in the electromagnetic spectrum between the far-IR and the microwave region with frequencies between 20 and 0.1 THz or 15 µm to 3 mm wavelength. However, only the lower frequency region is commonly exploited in the analysis of pieces of art. Due to the lack of practical sources and detectors THz radiation was until recently not exploited in spectroscopy, leading to what is called the “Terahertz gap”, but progress in instrumentation has closed this gap in the last two decades [153].

THz radiation is suitable for the investigation of sub-surface features of historical paintings as most materials, with the notable exception of metals and water, absorb THz radiation only weakly and allow for information depths in the millimetre range or larger. The use of THz radiation for the investigation of cultural heritage objects has been recently reviewed by Jackson et al. [7].

THz spectroscopy allows for the probing of intermolecular interactions such as hydrogen bonds. It is worth noting that the spectral features observed in the THz range are commonly not scientifically explained, but allow for a distinction between different pigments and binders. Spectral databases for THz radiation large enough to allow for a reliable identification of unknown compounds are still missing, but are in development [154]. Recently, THz spectroscopy has been proposed as a suitable tool for the study coal tar dyes [28].

Most imaging experiments using THz radiation for the investigation of paintings employ time domain spectroscopy (TDS-THz), typically limited to the energy range of 0.1-3 THz. In these instruments the sample is scanned with short THz pulses derived from femtosecond lasers, either in reflection or transmission geometry. The laser used to generate the THz pulse is split in order to acquire the waveform of the THz pulse after interaction with the sample in a pump-probe scheme.

Both signals, transmitted and reflected, contain information about the absorption characteristics of the material. Further, THz pulses are reflected on the interfaces between the layers if their optical properties in the THz range are different. So the thickness of layers can be determined from the time-of-flight of the THz pulse in reflection geometry. This allows, similar to OCT, the non-destructive acquisition of depth profiles, virtual cross sections and 3D data sets and due to the more penetrative nature of THz radiation these information is not limited to the surface layers. Modern instruments allow for the acquisition of up to 1000 waveforms per second, although
several waveforms might need to be acquired on the same location to improve the statistics of the measurement [7].

The lateral resolution of these systems is determined by the diffraction limit of the radiation employed but was reported as low as 220 µm [155]. Different groups calculated that the minimum thickness of a layer in a historical painting to be detected in a depth profile is 40-50 µm [155, 156]. The extraction of absorption spectra from reflected waveforms is possible, but in the spectral region up to 3 THz only few pigments feature characteristic bands. The separation of different components from the absorption spectra acquired in transmission by component spatial pattern analysis is discussed in [157].

Different test objects, either self made or real artefacts of low value have been investigated by THz. Köhler et al. described in 2006 transmission experiments on a painting made with materials typical for the 19th century [53]. Adam et al. studied hidden raw umber layers covered by lead white in mock-up samples in reflection geometry through the canvas [156]. Abraham et al. investigated the possibility of visualizing graphite underdrawings in test samples [158]. It has to be pointed out the study of 16th century underpainting by THz radiation is more problematic, as the carbon-based black pigments commonly employed are only weakly absorbing the THz radiation as opposed to graphite. Further, TDS-THz has also been proposed for the study of tree rings in painted wood [159], the detection of delaminations [160] and for the detection of defects in a painted wooden panel [161].

Funkunaga et al. investigated the Polittico di Badia by Giotto di Bondone (1266-1337) from the collection of the Galleria degli Uffizi (Firenze, IT) [154, 160]. In this case THz spectroscopy succeeded in determining the extension of cracks in the support of the panel painting, confirming the presence of a cloth in the painting’s ground and in imaging the application of gold leafs in the painting (see Figure 9).
Instead of using pulsed THz sources continuous wave (CW) sources can be employed to create waves in the lower frequency range (~ 0.2 THz). While in this case only the transmitted or reflected intensity is measured and neither depth information nor spectra are acquired, CW systems are simple and fast (several pixel/s) [162]. Younus et al. obtained promising results by visualizing graphite sketches under paint layers in transmission and reflection geometry with a CW instrument. Further, the investigation of various archaeological artefacts by THz radiation is described [163]. While CW THz imaging allows for the straightforward investigation of historical paintings its lateral resolution is limited to the range of several millimetres due to the long wavelength of the primary radiation. However, higher frequency CW sources based on quantum cascade lasers have been described, but to my best knowledge not used for the investigation of historical paintings [164].
1.6 Unilateral NMR

In Nuclear Magnetic Resonance spectroscopy (NMR) the relaxation of a sample’s magnetization in a strong magnetic field after excitation by a radio-frequent pulse is measured. The relaxation time is dependent on the direct surrounding of the excited nuclei and thus gives insight in the sample’s chemical structure. NMR has been applied in a wide range of studies in the field of cultural heritage analysis [10].

Unfortunately, the instrumentation commonly employed for NMR measurements is not suitable for the in-situ investigation of historical paintings, as, in order to obtain a homogeneous magnetic field, the sample is placed inside the (circular) magnet of the instrument in a volume too small to contain a painting. In-situ measurements became feasible with the development of the NMR-MOUSE, a mobile stray-field NMR system sensitive to $^1$H nuclei in that the investigated volume is positioned in front of the instrument [165].

The investigated volume has a size of ca. 10x10 mm$^2$ and a depth resolution of less than 10 µm can be achieved. As paint layers commonly are not perfectly flat and signals from a large volume are recorded this resolution is commonly not achieved in real samples. Depth profiles are acquired by changing the distance of instrument to painting via a motorized stage. The maximum sampling depth is 25 mm [52, 166]. The acquisition of a depth profile necessitates 30-40 minutes, so that 3-dimensional mapping of a painting is not practical. Further, care must be taken if nails or other iron parts are near the analyzed spot, as the attractive forces between the magnet and painting may be the cause of unfortunate accidents.

While the homogeneity of the magnetic field is insufficient to acquire spectroscopic information that allow an identification of the compounds present, NMR depth profiles provide valuable information. The amplitude of the measured signal is proportional to the abundance of $^1$H nuclei in the investigated volume, so that the distribution of organic compounds (e.g. varnish, binders and canvas) and water in covered layers can be investigated. The latter is, of course, more of interest in frescos than in easel paintings. This constitutes a major advantage as most techniques that allow to study these compounds in a non-invasive fashion are only surface sensitive. NMR depth profiles have been employed to investigate the presence and thickness of canvas reinforcements (inacamottatura) in a 15th century panel painting [52], paint layer thickness [166] and to compare the binder used in paint and priming layer of a painting by Alberto Burri [166].
Further, the measured relaxation times of the nuclei are related to the age of a paint layer, as its brittleness and the molecular mobility in it change over the years. So a correlation between relaxation time and age of paintings can be observed, which may be exploited to distinguish between old and recently added paint [166].
1.7 Non Destructive Testing

The conservation of paintings shares some common ground with classical engineering when it comes to the detection of sub-surface defects by Non Destructive Testing (NDT). Some of the methods devised for testing and quality control in the industry have been applied on historical paintings. The results of these methods are of great interest to painting conservators as they allow to localize defects in the painting at an early stage, even before they become apparent on the surface of the painting. Next to archiving the state of conservation of the painting, these methods allow to monitor the changes during unusual events (e.g. transport) and over a prolonged time. Instrumentation made for NDT is commonly easily transportable, allowing for in-situ investigations.

These techniques are in general suitable for detecting delaminations. A kind of defect that, as opposed to cracks, is difficult to detect with the established imaging techniques XRR and IRR and is commonly studied by the visual observation of slight irregularities in the surface of a painting. Further, the so called percussion method has been described, in that the sound emitted by the painting upon a slightly tapping on the surface is interpreted [13, 167]. The investigation of cultural heritage objects by NDT has been reviewed a few years ago [11].

1.7.1 Holographic and speckle methods

Laser based holographic and speckle methods (Holographic Interferometry (HI), Electronic Speckle Pattern Interferometry (ESPI), Electronic Speckle Pattern Shearing Interferometry (ESPSI or Shearography) and Speckle decorrelation) allow to visualize minor displacements of a surface under stress. The methods utilize laser light in the optical range to illuminate the painting’s surface and acquire images in full-field mode. In case of HI and ESPI the interference pattern of the acquired image with a reference beam is recorded, while in case of shearography the acquired image is split and the interference between the original image and its sheared version of it is recorded. Two optical representations (holograms or speckle patterns) acquired before and after the loading (i.e. putting the painting under very slight stress) are superimposed (in case of holograms) or subtracted (in case of speckle patterns) yielding correlation patterns that indicate the surface displacement. Surface and sub-surface defects, such as voids, cracks and delaminations, can be visualized in these patterns as they create discontinuities in the patterns formed by influencing the deformation of the paint surface. A fringe pattern indicating a sub-surface defect is shown in Figure 10.
The *loading* of the painting is commonly done either by irradiation with IR radiation or a stream of warm air. The temperature change necessary is a few degrees and below normal temperature fluctuations in a museum. Also *loading* by sound waves and mechanically, e.g. by vibration, has been described. The normal temperature and humidity variations can result in significant deformations that are exploited in *ambient loading* [168].

The first application of HI was already described in 1974 by Amadesi et al. [54]. Recently, the application of these techniques for the inspection of works of art was reviewed by Tornari [12] and Ambrosini et al. [13]. Recent progress in the interpretation of the fringe patterns obtained with these methods was described by Tornari [169].

All of the methods mentioned above have been used for *in-situ* investigations, although HI, which yields the best results of the methods mentioned, is less well suited for this due to its sensitivity to vibrations.

The capabilities of the techniques were recently demonstrated in a *in-situ* study of the influence of changed climatic conditions induced by a heating system on a painted wooden altar in Norway, employing Speckle decorrelation and EPSI [167]. A similar study highlighted the capability of HI to evaluate defects created (or healed) in a painting during transport to an exhibitions and restoration treatments [170].
1.7.2 Ultrasonic
The application of ultrasonic techniques in that the propagation of sound waves in the wooden support of a panel painting is measured, was first described in 1996 [56]. The ultrasonic methods applied for the investigation of paintings have been recently reviewed and encompass next to air coupled (or non-contact) ultrasound scanning, also contact ultrasound and acoustic microscopy [171].

Non-contact, scanning instruments that allow the visualization of defects in the structure of panel painting have been described in transmission and reflection geometry. In the obtained images delaminations and cracks in ground and wooden support can be localized. The lateral resolution is given as several millimetres, depending on the experimental conditions, while no depth information is obtained [172].

Acoustic microscopy allows for the non-destructive acquisition of 3-dimensional data sets of paint layers with micrometer resolution. Its application on paintings is limited by the fact that a direct contact between transducer and painting is necessary, employing contact gel or other liquids [171]. Karagiannis et al. [173] described the development of an acoustic microscope for the analysis of painted art objects and achieved promising results on a range of test samples by dedicated data treatment.

Sfarra et al. described a simple ultrasonic system for the detection of subsurface defects in paintings. In this system transducer and receiver are placed manually on the surface of the object. It also requires contact gel in case of none flat surfaces. While the system is not capable of acquiring images it allows to localization of defects by manually performed line scans [174].

1.7.3 Thermography
In thermography the (MIR range) thermal radiation emitted by a sample is recorded in order to obtain temperature maps that reveal surface and subsurface features. While for the study of buildings passive thermography is sufficient, paintings need to be actively warmed for thermographic experiments. Already in the 1970s active thermography was proposed for the investigation of panel paintings [55]. Its application for the investigation of cultural heritage objects has been recently reviewed [14].

Pulsed thermography is commonly employed for the analysis of paintings. In this technique the surface of the painting is warmed by a few degrees with a heat pulse. The thermal radiation of the heat pulse is absorbed in the surface layer(s) and propagates into deeper layers, the ground and the support. The air-pockets in delaminations and other discontinuities
constitute thermal insulators that hinder the heat propagation, so that paint layers above them cool down slower compared to intact areas. The temperature of the painting’s surface is estimated by recording the thermal radiation emitted by it with IR cameras sensitive in the spectral region above 3 µm.

The amount of thermal radiation emitted does not only depend on sub-surface defects, but also on the absorption of the heat pulse in the paint layers and the emissivity of the material present. This can result in the misinterpretation of strongly emitting retouches as delaminations [175], on the other hand it allows the visualization of strongly IR absorbing underdrawings and signatures [176-178]. Advanced data processing techniques such as Pulse Phase Thermography, Principal Component Thermography and Differential Absorption Contrast enhance the readability of the thermograms and allow, if the materials present in the painting can be determined, an estimation of the depth of a defect under the painting surface [178].
1.8 Conclusions and Outlook

25 years ago the only *in-situ* techniques for the investigation of covered paint layers in historical paintings were XRR and IRR. The first allows for the visualization of strongly X-ray absorbing features, such as thick layers or layers containing heavy elements. The second allows for the visualization of carbon-based black pigments. Covered layers not belonging to one of these groups were very difficult to investigate without taking samples or transporting the painting for NAAR to a nuclear research reactor. Both techniques are established in the investigation of paintings and practiced in conservation studios and museums on a routine base. Most investigations of historical paintings start, after a close visual inspection, with XRR and possibly IRR as this is a fast straightforward procedure. Areas of interest identified in these early investigations can then be examined with more advanced techniques to answer open questions.

In both techniques, XRR and IRR, digital detection systems have been introduced, allowing for faster acquisition and data processing. The contrast obtained by XRR has been improved by various methods, such as strati-radiography and electron emission radiography, that reduce contributions from the painting’s support. Promising early results have been obtained by energy resolved XRR, but until now no results of important pieces of art obtained with X-ray tube based instruments have been presented.

CT and CL allow for the acquisition of 3-dimensional data sets of paintings, instead of 2-dimensional projections. While CT is useful for studies of the support of panel paintings, CL allows for the acquisition of high resolution 3-dimensional data sets of the paint layers. However, for the later no instruments suitable for the investigation of paintings have been described outside of synchrotron sources.

Multi-spectral IRR has proven its value for the investigation of sub-surface layers, as it allows to select the wavelength yielding the best contrast in a given combination of ground material and pigments. Further, multi-spectral IRR allows for the identification and mapping of pigments on the surface of a painting, if used in combination with spectral databases and complimentary methods.

Unilateral NMR yields very limited, but unique information. No other technique allows to obtain $^1$H abundance depth profiles. The approach of dating a painting by the molecular mobility in its paint layers is promising, but still needs to be validated in coming studies.

OCT allows for the non-destructive acquisition of virtual cross-sections in paintings and IRR images with enhanced contrast and resolution. The
method is limited by the strong absorption of the employed radiation in the paint layers and the fact that little information beyond the location of interfaces in the paint layers are obtained. However, the mature instrumentation allows for a straightforward application of the method that can often render sampling unnecessary.

As most materials are only weakly absorbing THz radiation it is well suited for the investigation for the interior of cultural heritage objects. Virtual cross-sections and absorption/reflection images allow to visualize layers not detectable by other methods. Progress in instrumentation is expected to enhance the capabilities of THz imaging considerably. Especially an extension of the spectral range available for spectroscopy would be desirable.

Laser based NDT techniques and thermography have long been available for \textit{in-situ} measurements and have proven their worth for the analysis of paintings. Their results allow for an early and reproducible identification of sub-surface defects in paintings and considerably contribute to the planning conservation treatments. While the application of ultrasound microscopes is hindered by the need for direct contact to the surface, simple air-coupled ultrasound systems allow for the non-contact detection of delaminations in panel paintings.

None of these techniques is capable of acquiring elemental distribution images \textit{in-situ} with effort comparable to MA-XRF. NAAR (see Chapter 5) is not capable of \textit{in-situ} investigations and energy resolved radiography is still in development. Further, its transmission geometry complicates the application and strongly absorbing supports prohibit it. However, MA-XRF also has several limitations. Next to self-absorption effects complicating the clear visualization of covered paint layers, MA-XRF only provides 2-dimensional projections with only limited depth information (see Chapter 3). These can be provided by OCT and Terahertz imaging. MA-XRF can only detect elements heavier than S and not distinguish directly between pigments consisting of the same elements detectable by XRF. IRR and multispectral imaging in the IR range allow for the visualization of hidden layers executed in pigments only weakly or not detected by MA-XRF (e.g. carbon-based blacks) and to identify compounds at the surface of paintings.

Given the unique information obtained by MA-XRF and its ease of application it has developed in the last five years from a highly experimental method limited to SR sources to a commercially available method for the \textit{in-situ} use.

This chapter is based on the submitted manuscript [179].
1.9 References


M. Radepont, W. De Nolf, K. Janssens, G. Van der Snickt, Y. Coquinot, L. Klaassen, M. Cotte, The use of microscopic X-ray diffraction for the study of HgS and its degradation products corderoite (α-Hg₃S₂Cl₂), kenhsuite (γ-Hg₃S₂Cl₂) and calomel (Hg₂Cl₂) in historical paintings, J. Anal. At. Spectrom. 26 (2011) 959-968.


Ruggieri, G. Ghia (Eds), Caravaggio. La tecnica e lo stile, Silvana Editoriale, Cinisello Balsamo (Milan), 2013 (accepted).


Chapter 1 – Introduction


Chapter 3 – Data processing

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2 Instrumentation

2.1 Introduction
The development of instruments for the acquisition of elemental distribution images via XRF imaging was the central part of this project.

The first experiments, employing synchrotron radiation (SR), were performed at beamline L of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen Synchrotron (DESY) in Hamburg, Germany, where already the first successful MA-XRF investigation of a painting was executed [1]. This instrument was improved in this project by the introduction of the use of four detectors. Further experiments were done at beamline X7A of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL) in New York, USA. Here use was made of a (early) prototype of the Maia detector, which allows to record high intensity fluorescence radiation within a large solid angle.

The pigments used to create a painting are generally present at a concentration level of several mass percent. By employing high intensity SR to scan a painting, the heavy elements present in the paint can be visualized with dwell times far below one second. However, also a well-designed X-ray tube based system can be sensitive enough to image their distribution. So, in parallel to the synchrotron experiments several mobile scanners were constructed at the University of Antwerp, labelled Instruments A to D. Furthermore, the first commercial XRF scanner for the investigation of historical paintings, the Bruker M6 Jetstream, was employed for the analysis of a number of paintings.

The first mobile scanner (Instrument A) was constructed by re-configuring the components of an existing scanning micro-XRF set-up. While its sensitivity and the range of its motorized stages was unsatisfactory, it confirmed that even with simple, X-ray tube based systems, the investigation of paintings is possible. To allow for faster scanning of larger areas, Instrument B and C were constructed. These instruments employed four detectors, motorized stages with a larger travel range and new X-ray sources. The main difference among them resided with the beam defining optic employed. While Instrument C used a polycapillary optic to obtain a beam size of a few tens of micrometers, Instrument B used a simple Pb pinhole collimator that allowed for a more efficient excitation of heavy elements. Finally, the detectors of Instrument B were rearranged tightly around the X-ray source, yielding Instrument D, today the most sensitive mobile MA-XRF scanner.
The work on mobile MA-XRF scanners culminated in the M6 Jetstream by Bruker Nano GmbH (Berlin, Germany). The development of this first commercial system for the investigation of historical paintings by MA-XRF was based on the technology of the Bruker M4 Tornado and our experience gained with the in-house built Instruments A to D.

In general, an XRF scanner consists of an X-ray source, a beam defining optic, one or more energy dispersive detectors and a motorized stage, moving either the measurement head or the sample (see Figure 11). Furthermore, dedicated software to control the operation of the different components is needed.

**Figure 11 Schematic of an XRF scanner.**

Every imaging experiment attempts to achieve the highest lateral resolution and the best quality of the image, i.e. high contrast and low noise/artefact level. As the time for an experiment is in general limited, compromises between measurement time, resolution and image quality have to be made.

The lateral resolution achieved is defined by the pixel size of the scan and the beam size. Ideally, pixel size and beam size are identical. Acquisition of data with a beam size larger than the pixel size is called *oversampling*, while the contrary is labelled *undersampling*. *Oversampling* results in a blurred image, as the spectra of several pixels of the final image are recorded simultaneously and saved in the central pixel (this can be observed in the middle column of Figure 33). *Undersampling* yields sharp images, but it is possible to miss local in-homogeneities. *Undersampling* is often not problematic in the MA-XRF analysis of paintings, i.e., when the
features of interest are larger than the pixel size. One has to be aware that in order to improve the lateral resolution by a factor of two the number of pixels is squared and with it the corresponding time needed for the measurement.

The more photons of a characteristic X-ray fluorescence line are recorded, the lesser the relative statistical fluctuations and the better interferences with other lines or the spectral background can be resolved. The statistical fluctuations on the net intensity of element \( N_i \) can be estimated by assuming Poisson statistics.

\[
\sigma(N_i) = \sqrt{N_i} \tag{Eq. 2.1}
\]

Thus, doubling the number of recorded photons will yield a 41% better image in terms of statistical fluctuations. This can be achieved either by doubling the measurement time, doubling the sensitivity for the element in question or a combination of both. The number of recorded photons of transition \( k \) to shell vacancy \( j \) of element \( i \) is given in Eq. 2.2.

\[
N_{ijk} = t \cdot m_i \cdot Y_{ijk} \cdot A_{ijk} \cdot A_{ijk}' = t \cdot m_i \cdot \frac{\Omega}{4\pi} \cdot \varepsilon(E_{ijk}) \cdot \omega_{ij} \cdot p_{ijk} \times \int_{E_{ij}^\text{edge}}^{E_{\text{max}}} I_0(E) \cdot \tau_{ij}(E) \cdot A_{ijk}(E) \cdot A_{ijk}'(E) dE \tag{Eq. 2.2}
\]

where \( N_{ijk} \) is the number of recorded photons, \( t \) is the measurement time, \( Y_{ijk} \) is the sensitivity, \( m_i \) is the mass of element \( i \) in the beam, \( \Omega \) is the solid angle within that radiation is recorded by the detector(s), \( \varepsilon(E_{ijk}) \) is the detector’s efficiency for the energy of the emitted fluorescence energy, \( \omega_{ij} \) is the fluorescence yield and \( p_{ijk} \) the transition probability of the measured transition. \( E_{ij}^\text{edge} \) is the energy of the elements absorption edge and \( E_{\text{max}} \) the maximum energy of a photon emitted from the source. \( I_0(E) \) is the intensity of the primary beam, \( \tau_{ij}(E) \) is the energy dependent elemental photoelectric cross section, \( A_{ijk}(E) \) is the self-absorption term and \( A_{ijk}'(E) \) is a term taking the absorption outside of the sample into account. Both absorption terms will be discussed in detail in Chapter 3.

The irradiated mass of element \( i \) can be described by

\[
m_i = w_i \cdot \left( \frac{b}{2} \right)^2 \cdot \pi \cdot \frac{d}{\sin(\alpha)} \cdot \rho \tag{Eq. 2.3}
\]
with \( w_i \) the weight fraction of element \( i \), \( b \) the beam diameter, \( d \) the thickness of the sample, \( \rho \) the density of the sample and \( \alpha \) the angle of incidence of the primary beam (see Figure 15). These fundamental parameter calculations were described in detail in [2].

It is obvious that \( \omega_{ijk}, p_{ijk} \) and \( \tau_j \) are physical constants that are not changed by the experimental conditions. \( w_i, d \) and \( \rho \) are properties of the sample that also are not changed in non-destructive investigations. \( A_{ijk} \) and \( A'_{ijk} \) are largely dependent on the sample, but also on the measurement geometry (see below). \( t \) can be adjusted to record a larger number of photons, but it is not recommended, as time is one of the very few things that cannot be bought, as opposed to spectrometers and their components. The other variables can be influenced by the design of the instrument. \( I_0(E) \) and \( E_{\text{max}} \) are dependent on the radiation source employed and influenced by the beam defining optic. The beam defining optic also defines the beam diameter \( b \). \( \varepsilon(E_{ijk}) \) is dependent on the detector chosen, which also limits the maximum possible value of \( \Omega \). Furthermore, \( \Omega, I_0(E), b \) and \( \alpha \) are dependent on the measurement geometry.

2.1.1 Radiation sources

In this work two different types of radiation sources were used: X-ray tubes and SR sources.

An X-ray tube consists of an evacuated chamber in which an anode and cathode are present. If a high voltage is applied between the two (several tens of kV) electrons are emitted from the cathode and impinge on the anode, where they are suddenly decelerated. Usually electrons are thermally emitted from a heated cathode wire, called the tube filament. The energy lost by the electrons is converted to heat and is emitted in the form of a continuum of X-rays, the bremsstrahlung. Next to the bremsstrahlung the impinging electrons also create inner shell vacancies in the atoms of the anode material, exciting them to emit their characteristic fluorescence lines. The latter only occurs if the energy of the electrons is higher than the respective absorption edge of the anode material. Commonly, the X-rays leave the tube through a thin Be window, but also transmission tubes, where a thin metal foil serves both as anode and exit window, were employed. The maximum energy of a photon emitted by an X-ray tube is defined by the voltage applied. Furthermore, the number of photons emitted for a given energy is proportional to the difference to the maximum energy. The X-rays reaching the sample are attenuated by the
exit window and the air, so that their low energy component is considerably reduced. The shape of the bremsstrahlung continuum is shown in Figure 12.

Given that only photons with an energy higher than the absorption edge excite an element, it is recommended that the voltage the X-ray tube is operated at ca 1.5-2 times the energy of the absorption edge of the element of interest [3].

![Bremsstrahlung continuum of a Rh-anode X-ray tube operated at 45 kV after passing through 5 cm of air. Calculated with PyMCA [4] based on a work of Ebel [5].](image)

SR is emitted when light particles (electrons or positrons) at relativistic speed (i.e. close to the speed of light) are forced to change their direction. In a synchrotron storage ring, the particles are accelerated by bending magnets towards the centre of the ring, so that the SR is emitted tangentially to the ring. SR spans a broad energy range from the infrared to the X-ray region.
The first generation of synchrotron radiation sources were designed for particle physics experiments. SR was an unwanted by-product that could be used only in “parasitic” mode. The second generation synchrotron radiation sources were storage rings designed for the emission of synchrotron radiation from the bending magnets of the storage ring. The third generation utilizes insertion devices (e.g., wigglers, undulators) instead of bending magnets, enhancing the brightness of the X-ray sources considerably. The fourth generation of SR sources moves away from storage rings to linear accelerators, yielding pulsed bursts of high brilliance [6].

In this work only SR from the bending magnets of second generation synchrotron sources was used.

SR is guided from the storage ring to the experimental station via a beamline, an evacuated tube. Both experimental station and beamline are shielded to protect the operators from the health hazards of ionizing radiation. The experimental station commonly includes a monochromator based on Bragg’s law, employing two crystals or multilayers of different materials. SR sources are immobile, so that the painting for analysis needs to be brought to them, but have several distinct advantages over X-ray tube sources [7]:

1. Their primary radiation is several orders of magnitude more intense than the radiation emitted by X-ray tube sources. It is so high, that one even can afford losing most of the intensity in a monochromator in order to yield quasi-monochromatic beams.
2. SR is highly parallel, so that it is easier to focus and collimate than X-rays emitted from an X-ray tube.
3. SR is linear polarized, so that a detector placed at 90 degrees to the incoming beam in the plane of the ring records only a minimum of scattered radiation, reducing the spectral background in the acquired spectra. This effect was only exploited during the experiments performed at the NSLS.

The primary radiation indirectly influences the beam size in connection with the beam defining optic (see there), but its main influence on the count rate obtained is the intensity of the primary beam $I_0(E)$.

It is obvious from Eq. 2.2 that the detected XRF count rate rises with $I_0(E)\cdot \tau_{ij}(E)$. The photoelectric cross-section $\tau_{ij}(E)$ is element specific and energy dependent. It takes its largest value directly above the absorption edge $E_{ij}^{edge}$. So, a general enhancement of the primary beam’s intensity
would enhance the count rate for all elements, while an enhancement of the primary beam in the energy region directly above an element’s absorption edge would allow enhancing the sensitivity for this element more than for the other elements in the sample.

The primary radiation emitted by X-ray sources can be modified by placing filters in the primary beam. However, as the detectors in the mobile instruments were not saturated during the measurement of historical paintings, this brought no advantage in terms of sensitivity and was not done.

Only in a few experiments use was made of white SR. Commonly, monochromatic SR was used with an energy slightly above the edge of the heaviest element of interest.

### 2.1.2 Beam defining optics

Three kinds of beam defining optics were used in these experiments: Collimators, polycapillary lenses and a combination of focussing monochromators and mirrors. Simple collimators, consisting either of Pb pinholes or slit systems were the most used optics, while the focussing monochromator and mirror optics were used in a single experiment.

Collimators are small and easy to mount and align in the beam. However, once the collimator is manufactured its diameter cannot be adjusted. Slit systems allow to freely adjust the size of the beam employed. As they are rather large and heavy, they found no application in the mobile instruments. The divergence of the yielded beam is source dependent. SR is in the experimental hutch a largely parallel beam, so that only a low divergence is observed. With X-ray tubes more divergent beams are obtained. X-ray tube, collimator and sample need to be relative close to each other to utilize as much as possible of the radiation emitted by the X-ray tube and still yield a beam in the size of the collimator opening. As the flux (number of photons) of the beam passing through a collimator is directly proportional to the area of the opening, the sensitivity increases as described in Eq. 2.3.

Polycapillary optics consist of an assembly of monocapillaries. Polycapillaries accept radiation from a large aperture and focus it into one small spot. The process is based on total external reflection of the X-rays on the walls of the capillaries. They allow producing micro-beams of several thousand times the intensity than what would be achievable with a collimator [8].

However, polycapillary lenses have several limitations:
1) They require precise alignment.
2) While polycapillaries enhance the intensity of the beam, they also result in a strongly divergent beam.
3) The angle of total reflection is energy dependent, resulting in an energy dependent beam size, which can induce chromatic aberration in the images obtained.
4) The transmission of polycapillary lenses is energy dependent so that they effectively act as a filter to the primary radiation, especially in the region above 20 keV.

Due to point (1), the polycapillary optics used in this work were fixed to the X-ray tubes of Instrument C and the M6 Jetstream and aligned by the manufacturer, so that no misalignment, e.g. during transport, occurred.

2.1.3 Detectors
All detectors used in this work are based on high quality Si crystals on to which a voltage is applied. As no charge carriers are present in the crystal, no current is observed beyond thermally generated charges, which numbers are reduced by cooling the crystal. In the detectors used, the active volume in which the X-rays are detected has a thickness of several hundred micrometers and an active area in the order of several (tens of) square millimetres.

X-rays normally interact with the crystal by photoelectric absorption to create an inner-shell vacancy in the semiconductor material together with an energetic photoelectron. This photoelectron interacts with the atoms in the active volume to produce multiple low-energy ionization events. The initial inner shell vacancy results either in an Auger electron or the emission of low energy X-rays. These and the photoelectron are absorbed in the active volume and create multiple electron-hole pairs. Due to these charge carriers the crystal becomes conducting and a current proportional to the energy of the initial photon can be measured. This current is amplified and shaped into a voltage peak. The voltage peaks of multiple events are converted into a spectrum in the pulse processor. Charge created in a thin layer on the surface of the detector crystal, the so called "dead layer", cannot be properly measured and is thus lost. On some detectors a thin gold contact layer (of a few tens of nm thickness) is present on the surface of the detector.

The detector electronics are not capable of processing more than one event at any given time, so that the detector becomes insensitive for short moments, the so called "dead time". It is commonly expressed as the percentage of time that the detector is not responsive and results in a discrepancy between the input rate $N_I$ (the number of events registered by
the detector) and the output rate $N_o$ (the number of events contributing to the spectrum). The output rate rises with the input rate until it reaches the inverse of the dead time constant $k$. From this moment on the output rate is actually decreasing with rising input rate. Very high input rates can completely saturate the detector, so that the output rate approaches zero (s. Figure 13).

![Graph showing the relationship between input rate, output rate, and dead time.]

**Figure 13 Relation between input rate, output rate and dead time.**

The detector electronics reject photons that are detected too close to one another to be separated, but in a small time window (in the range of 100 ns) this is not possible. Two photons being detected in this short time window are processed as a single event with the energy of both photons added up. A so called pile-up peak is recorded as the results of the detection of these coincident photons.

Further, there is a finite probability that the X-ray fluorescence photon resulting from the initial inner shell vacancy is not absorbed within the active volume, but “escapes” detection, resulting in an escape peak at the energy of the initial photon reduced by the energy of the escaped photon. In case of Si detectors this energy is the Si-$K_x$ line of 1.74 keV.

Another characteristic of the detector and its electronics is the energy resolution. In general it can be said, that the higher the energy resolution, the better interferences in the acquired spectrum can be resolved. The energy resolution and dead time are determined, next to instrumental constants, by the peak shaping time, a user defined parameter. The more
time per event is spent, the better the energy resolution achieved and also the higher the dead time.

Two variables in Eq. 2.2 depend on the detector: $\varepsilon(E_{ijk})$ and $\Omega$. The detector’s energy dependent efficiency $\varepsilon(E_{ijk})$ can be written as:

$$\varepsilon(E) = T_{Be}(E) \cdot T_{\text{dead layer}}(E) \cdot T_{Au}(E) \cdot (1 - T_{\text{volume}}(E))$$  \hspace{1cm} \text{Eq. 2.4}

with the energy dependent transmission $T(E) = \frac{I(E)}{I_0(E)} = \exp(-\mu(E)\rho d)$, $d$ thickness, $\rho$ density and $\mu$ mass absorption coefficient of the absorbing layer, $T_{Be}$ the transmission of the beryllium window of the detector, $T_{\text{dead layer}}$ the transmission of the insensitive “dead” layer on the sensitive volume of the detector, $T_{Au}$ the transmission of the (optional) gold contact on the detector crystal and $T_{\text{volume}}$ the transmission of the sensitive volume of the detector crystal [3].

In most experiments the Silicon Drift Detectors (SDDs) Vortex EX-60 and EX-90 (SII, Northridge, CA, USA) were used. According to the manufacturer, these detectors feature a crystal thickness of 350 µm, a 25 µm Be window, a dead layer of 0.05 µm and no Au contact layer. The detector efficiency for K$_{\alpha}$ and L$_{\alpha}$-lines for different elements is shown in the upper part of Figure 14, not including absorption in the air path, which is shown in the lower part of the same figure. The active area of the detectors was reduced by Ta collimators that covered the rim of the detector crystal to reduce the contribution of scattered primary radiation and the partial detection of X-rays. The 400 µm thick Maia detector features a similar efficiency curve. However, the design of the Maia prototype used results in an inefficient response to radiation of low energy, so that the K-lines of elements lighter than Ca (Z=20) are only weakly detectable.

The detector’s efficiency is optimal for elements between Ca (Z=20) and Zn (Z=30) for K-lines and between Cd (Z=48) and Pb (Z=82) for L-lines. These elements are often of interest in the investigation of historical paintings. However, fluorescence lines with energy below 5 keV are often not observable in covered paint layers, so that for the study of elements with L-lines in this region, the detection of K-level fluorescence is preferred. The detection of the K-lines of Cd (Z=48, Cd-K$_{\alpha}$=23.1 keV), Sn (Z=50, Sn-K$_{\alpha}$=25.2 keV) and Sb (Z=51, Sb-K$_{\alpha}$=26.3 keV) is feasible, albeit with a comparably low efficiency. For most elements air-absorption is no
large concern, but for the detection of lighter elements, such as Ca (Z=20) a short air path between sample and detector is recommended (see lower part of Figure 14).

Figure 14 Above: Detector efficiency for Kα and Lα radiation of various elements. Below: Transmission of air for Kα and Lα radiation of various elements.

The active area of the detector also determines the maximum solid angle Ω from which the emitted radiation can be recorded. Furthermore, the distance of the detector to the sample influences Ω, as do collimators mounted in front of the detector.

It is obvious that in order to obtain the highest sensitivity ε(Eijk) and Ω should be enhanced as far as possible. However, the dependency of the dead time on the input rate complicates the decision. If high intensity primary radiation (e.g. as at a SR source) is employed, detectors with a large Ω are easily oversaturated.
One approach to prevent this is to modify $\varepsilon(E_{ijk})$ by the application of filters before the detector. By reducing $\varepsilon(E_{ijk})$ for matrix elements, the sensitivity for trace elements can be enhanced. This is suitable in case of biological samples, as the contribution of light elements needs to be reduced [9], but was not found useful in the analysis of paintings.

Beyond the constants $\Omega$ and $\varepsilon(E_{ijk})$, other characteristics are of great importance in the selection of the detector, such as the method of cooling of the detector (e.g. liquid nitrogen or a Peltier element), its weight, dimensions and its price.

During the experiments at the DESY synchrotron, an oversaturation of the detectors was avoided by reducing $I_0(E)$ with filters placed in the primary beam. At NSLS a more elegant solution was found. Here use was made of a prototype of the Maia detector, which is a dedicated detector for SR-based XRF. The prototype Maia detector consists of 96 detectors, each with 1 mm$^2$ of active area [10, 11]. The limited size of each detector element makes it less prone to being oversaturated than a single SDD with a larger active area; taken as a whole, the Maia detector allows to record the fluorescence radiation from a large solid angle. Despite the high sensitivity of the Maia, the prototype used in these experiments was hindered by its energy resolution that is still significantly worse than that of a SDD. Furthermore, the Maia has a low response to low energy radiation, so imaging of elements lighter than Ca by their K-shell fluorescence is normally not possible [12].

2.1.4 Geometry

The influence of the distance of X-ray source and detector to the sample has been discussed above, but also the angle of the incidence of the primary radiation $\alpha$ and the take-off angle of the emitted radiation $\beta$ are of importance (see Figure 15a). A small $\alpha$ results in a larger volume of the surface layer being excited, but at the price of lateral resolution, as the beam footprint is stretched in one dimension. Furthermore, if the primary beam is not incident at normal angle, the profile of the sample’s surface can result in a seemingly shifted beam position and shadowing effects. This is illustrated in Figure 15b. The point of incidence is shifted by a larger distance ($d_2$) than the shift of the beam ($d_1$).
Of most importance is the influence of the geometry on the sensitivity for covered layers. In general, the absorption in any homogeneous layer between the spectrometer and the sample with the mass attenuation coefficient $\mu$, thickness $d$ and density $\rho$ can be described by

$$A'_{ijk}(E) = \exp(-\chi(E, E_{ijk})\rho d)$$

with

$$\chi(E, E_{ijk}) = \mu(E) \frac{1}{\sin(\alpha)} + \mu(E_{ijk}) \frac{1}{\sin(\beta)}$$

It is obvious that to minimize the absorption in covering layers, $\alpha$ and $\beta$ should approach 90 degrees. In practice, this is difficult to achieve for geometrical reasons, but it was chosen to make $\alpha$ approach 90 degrees, to avoid the shift of beam position as mentioned above.

However, the instrument used by Howard et al. to analyze a painting by Arthur Streeton approached the optimal conditions of $\alpha$ and $\beta$ being equal to 90 degrees by guiding the primary beam through a aperture in the middle of a 384 detector element version of the Maia detector [13].

### 2.1.5 Control software

Elemental distribution images are acquired by scanning the surface of the painting with an X-ray beam and acquiring for every pixel in the image an XRF spectrum. While manufacturers commonly provide drivers and often simple GUIs for the control of their products, the coordination of all components of a spectrometer requires in-house written control software. The control software of Instruments A to D was obtained by modifying existing control software, written by B. Vekemans (University of Gent, formerly University of Antwerp). The control software of the other instruments was used as provided by the manufacturer.
Figure 16 Typical artefacts of dynamic scanning with position and time trigger. The images were corrected for by interpolating the affected pixels with the recorded intensity values in the lines above and below.

Acquisition of an elemental distribution image is either done by static scanning, in which the motorized stage is stationary during the acquisition of a spectrum, and dynamic scanning in which the beam is moved over the surface of the painting at a constant speed and the photons recorded from the area of the pixel are integrated into the spectrum corresponding to that pixel.

Static scanning is easy to implement in the control software, as no parallel operation of sub-components is necessary. However, the stopping, accelerating and stabilizing of the motorized stages introduces a mechanical dead time in which the scanner is not acquiring data. This is acceptable, as long as this additional dead time is much smaller than the acquisition time per pixel. In the first half of this project (until the fall of 2010) all scans were done by static scanning.
Dynamic scanning is more difficult to implement, as the spectra need to be read-out from the detector electronics while the motorized stages are in motion. Dynamic scanning can either be realized by triggering the saving of a spectrum after a pre-set time or by monitoring the position of the motor and triggering whenever the beam leaves a pixel. A time trigger is used in the M6 Jetstream and DESY scanner, a position trigger in the AXIL scanners. Both approaches introduce artefacts that need to be corrected in post processing. If a time trigger is used and a delay occurs, all following pixels are shifted. If a position trigger is used, the signals of several pixels are summed into a single pixel and the following pixels are not recorded, as the beam has already passed their trigger positions (see Figure 16).

Currently the control software of scanners is a serious bottleneck in performance. Given the sensitivities of the instruments discussed below, exposure times of a few milliseconds are sufficient to acquire (mostly) noise free images of the main components present at a concentration level of several mass percent. Especially the in-house built scanners are limited to a minimum dwell time of 150 ms per pixel. The control software of the DESY scanner limited it to a minimum dwell time of 200 ms.

The M6 Jetstream features the opposite problem. The maximum dwell time per pixel is limited. The probability of a delaying event per time interval can be assumed to be at least partly independent from the speed of the motors and the dwell time. Thus, a longer dwell times results in a longer time per line and a higher probability of an artefact caused by a delay. Also, as the acquired data is not written to the hard disk, but kept in memory during the scan, the maximum number of pixels is limited.
2.2 The instruments used

The instruments used (see Table 3) were characterized by their spectrometric figures-of-merit, sensitivity and limits of detection, and their beam size. A detailed measurement of the beam size asks for several hours of scanning, a time commonly not available during measurements at SR-sources. Thus, these instruments were characterized rather roughly, essentially to assure that the beam size was not larger than the step size.

The spectrometric figures-of-merit were determined from a spectrum of Standard Reference Material (SRM) 611 Trace Elements in Glass manufactured by the National Institute of Standards and Technology (NIST). The reference material is a 1 mm thick glass disc containing a broad range of elements at a nominal concentration level of 500 ppm. The elements not certified by the manufacturer were taken from [14].

From this spectra the sensitivity (Y) and limits of detection (LOD) normalized for one second were calculated by means of equations Eq. 2.7 and Eq. 2.8:

$$Y_i = \frac{N_i}{w_i \cdot t}$$  \hspace{1cm} \text{Eq. 2.7}

where $N_i$ is the net intensity of the XRF peak of this element, $w_i$ is the weight fraction of element $i$ in the standard and $t$ the collection time of the measurement. The sensitivity is here expressed in counts per second (cps) per relative concentration unit in NIST SRM 611. The calculated sensitivity includes the effect of self-absorption in the standard. In Eq. 2.2 the sensitivity is defined as cps per absolute mass of element $i$. This difference is due to the fact that the absolute sensitivity is difficult to measure, as it requires a definition of the mass of the element in the beam, including all self-absorption effects and the beam size in the depth of the sample.

The limits of detection were calculated by employing:

$$LOD_i = 3 \cdot \sqrt{\frac{N_{back}}{N_i}} \cdot w_i \cdot \sqrt{t}$$  \hspace{1cm} \text{Eq. 2.8}

where $N_{back}$ is the intensity of the background below the peak in question and $N_i$ the net intensity of the peak. For the calculation of the background intensity, 4$\sigma$ of the Gaussian function fitted to the peak were taken as its width. The beam size was measured by scanning brass (Cu/Zn), Fe and Au wires of 25 µm diameter at variable distances to the measuring head. The Full-Width-at-Half-Maximum (FWHM) of the obtained profiles was taken as a measure for the beam size. The beam size was corrected for the wire thickness as described in [8].
### Table 3 Overview of the scanners used

<table>
<thead>
<tr>
<th>Source</th>
<th>Optic</th>
<th>Motor range</th>
<th>Beam size</th>
<th>Take off angle</th>
<th>Angle of incidence</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Instrument A</strong></td>
<td>Polycapillary/collimator</td>
<td>10x10x10 cm</td>
<td>&gt;50 µm</td>
<td>45</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>Instrument B</strong></td>
<td>Collimator</td>
<td>60x25 cm</td>
<td>~1 mm</td>
<td>45</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>Instrument C</strong></td>
<td>Polycapillary/collimator</td>
<td>60x60 cm</td>
<td>&lt;50 µm</td>
<td>90</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>Instrument D</strong></td>
<td>Collimator</td>
<td>80x60x7 cm</td>
<td>&lt;50 µm</td>
<td>60</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>M6 Jetstream</strong></td>
<td>Polycapillary</td>
<td>80x60x7 cm</td>
<td>&lt;50 µm</td>
<td>60</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>DESY</strong></td>
<td>Collimating slits</td>
<td>60x60 cm</td>
<td>~0.6 mm</td>
<td>90</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>NSLS-A</strong></td>
<td>Maia (96 elements)</td>
<td>60x60 cm</td>
<td>~100 µm</td>
<td>90</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>NSLS-B</strong></td>
<td>Maia (96 elements)</td>
<td>60x60 cm</td>
<td>~250 µm</td>
<td>90</td>
<td>26,36,39,45</td>
</tr>
<tr>
<td><strong>Hamburg</strong></td>
<td>Maia (96 elements)</td>
<td>60x60 cm</td>
<td>~250 µm</td>
<td>90</td>
<td>26,36,39,45</td>
</tr>
</tbody>
</table>

*Table 3: Overview of the scanners used*
2.2.1 Mobile Instruments

2.2.1.1 Instrument A

Instrument A (see Figure 17) was constructed by re-configuring the components of an existing scanning micro-XRF set-up. An air-cooled 60 W Kevex micro-focus X-ray tube (Kevex, CA, USA) with a Mo-target and a Vortex-EX60 SDD were mounted on an XYZ motorized stage (Micro-controle spectra-physics S.A, Evry, France) that allowed for a minimum step size of 1 µm. Although the nominal power of the Kevex X-ray tube was 60 W, it was never operated beyond 10 W to prevent excessive heating of the X-ray tube head. As beam defining optic, a polycapillary lens (XOS, NY, USA) was used, yielding a primary beam of around 50 µm at the focus. For painting scanning, usually the instrument was used in defocused mode, i.e., the distance between the lens-tip and the painting was typically 1 cm larger than the focal distance of the lens. Alternatively, a Pb pinhole collimator (of 700 µm diameter) was employed to define the primary beam size. Next to resulting in a less divergent beam, this also has the advantage that the higher energy components of the primary beam reach the painting and can excite the K-level of elements such as Ag, Sn, Sb and Ba. The beam size is given in Figure 18 and the spectrometric figures-of-merit are shown in Figure 20. The description of the scanner was adapted from [15] with permission of The Royal Society of Chemistry. Results obtained with this instrument were published in [12].
2.2.1.2 Instrument B

In Instrument B (see Figure 19), the Inspector DSP (Canberra Inc., CT, USA) used in Instrument A was replaced by a four-channel DXP-XMAP (XIA LLC, Hayward CA, USA) multi-channel analyzer to which 4 Vortex EX...
detectors (two of type EX60 and two of type EX90) each with 50 mm$^2$ active area were connected while the rather voluminous 60 W Mo-anode X-ray tube was replaced by a compact 10 W MOXTEK 50 kV “Magnum” X-ray tube (Moxtek, UT, USA) with Rh target. The 4-channel signal processing electronics did not only allow using four detectors in parallel, but also permitted faster data acquisition at higher count rates and lower dead time levels. In this system the beam was defined by means of a Pb collimator of 0.8 mm diameter. The detectors were mounted under angles of 26, 36, 39 and 45 degrees relative to the primary beam. Additionally, the motorized stages were replaced by horizontal and vertical stages of 60 and 25 cm travel range respectively (Micro-controle spectra-physics S.A, Evry, France), to allow for scanning of a larger area with a minimum step size of 10 µm. The spectrometric figures-of-merit of Instrument B are shown in Figure 20. The Pb collimator of Instrument B was re-used in Instrument D (see Figure 23). The description of Instrument B was adapted from [15] with permission of The Royal Society of Chemistry. Results obtained with this instrument are published in [16].

![Figure 20a Sensitivity for the early mobile scanners used in this project.](image)
Figure 20b Limits of detection (LOD) for the early mobile scanners used in this project. LODs were normalized to 1 s.

2.2.1.3 Instrument C

Instrument C (see Figure 21) exploited the strength of the motorized stage of Instrument B to integrate a heavier X-ray tube. A 50 W X-Beam Powerflux X-ray tube (XOS, NY, USA) with Mo-anode equipped with a dedicated polycapillary lens was integrated into Instrument C. The vertical motorized stage was replaced with a larger one with 60 cm travel range by the same manufacturer and in the course of this works the detection
geometry was slightly improved. Next to allowing for faster measurements the instrument also allowed for higher lateral resolution than Instrument B. It can be seen in Figure 23 that in the focus of the polycapillary a beam size of less than 50 µm is obtained for the Au-L\textsubscript{α} line (9.7 keV). After the focal point the beam emitted by the polycapillary lens extends with a divergence between 112 mrad for the Fe-K\textsubscript{α} line (6.4 keV) and 85 mrad (Au-L\textsubscript{α}, 9.7 keV). Instrument C was described in [15] and results obtained with it are published in [17].

2.2.1.4 Instrument D

![Instrument D](image)

**Figure 22** Instrument D. Left: Measurement head, right motorized stage and measurement head.

Instrument D is an advanced version of Instrument B. It uses the same X-ray tube, optic and detectors and the same motorized stage as Instrument C, including the upgrade to the 60 cm vertical stage. The detectors are arranged closely around the X-ray tube, recording X-rays from a large solid angle (see Figure 22). Beyond the 0.8 mm diameter collimator of Instrument B one of 0.5 mm diameter was employed. The second collimator was also slightly longer, yielding a divergence of only 33 mrad, as opposed to the larger pinhole with 51 mrad (see Figure 23). The spectrometric figures-of-merit are shown in Figure 24. Instrument D was described in [18].
Figure 23 Beam size of Instrument C and D. Beyond 8 mm distance the brass and Au wires were not optimally positioned.

2.2.1.5 Bruker M6 Jetstream

The Bruker M6 Jetstream was developed by Bruker Nano GmbH (Berlin, Germany) in close contact with the Universities of Antwerp and Delft. It is based on the technique of the Bruker M4 Tornado micro-XRF scanner and the experience gained with the previous in-house built instruments of the University of Antwerp. It is the first commercially available XRF scanner for large planar objects.

The M6 Jetstream consists of a measuring head that is moved over the surface of a painting by means of a X,Y-motorized stage (Figure 25). This motorized stage features a minimum step size of 10 µm and a maximum travel range of 80x60 cm (h×v). The exact distance between the measuring head and the painting is adjusted by a motorized stage of 7 cm travel range oriented along the Z axis. The measurement head travels within a metal frame that can be tilted in order to adjust it to the surface of a painting and to allow the analysis of horizontally positioned samples. The frame holding the motorized stage is mounted on a box containing the detector electronics, the motor control electronics and the high voltage generator of the X-ray tube. The electronics box itself is mounted on a wheeled platform that allows for easy transport over short distances and positioning with respect to the painting. The measuring head consists of a 30 W Rh-target micro-focus X-ray tube with a maximum voltage of 50 kV and a maximum current of 0.6 mA. The spectral range of primary radiation emitted from the X-ray tube can be modified by the use of 5 filters, mounted in a motorized filter wheel. The beam is defined by means of a polycapillary optic, allowing for a variable beam size (with ca. 40 µm as the smallest beam size—see Figure 26) as a function of the distance between
the painting and the measuring head. After the focal point the beam diameter extends with an divergence between 83 mrad (E(Fe-K\(_\alpha\))=6.4 keV) and 61 mrad (E(Au-L\(_\alpha\))=9.7 keV).

Two optical cameras with magnifying optics, focused on the surface of the painting at the near normal angle are mounted on the measuring head. The focal plane of the stronger magnifying camera can be manually adjusted in five steps and is used for controlling the distance from the measuring head to the painting and thus the beam size. The less magnifying camera can be used to automatically acquire mosaic images of the whole surface of the painting that allow direct comparison of these images with the elemental distribution images. Further, these mosaic images are used for defining the scanned area. For geometrical reasons the cameras observe the surface of the painting with a slight offset from the spot excited by the X-ray beam. This offset is automatically corrected for by the control software during measurement. The spectrometric figures-of-merit are shown in Figure 24. The description of the M6 Jetstream was adapted from [19] with permission of The Royal Society of Chemistry.
Figure 24 Sensitivity and limits of detection normalized to 1 s of the mature mobile scanners used in this project
Figure 25 Bruker M6 Jetstream. Reproduced from [19] with permission of The Royal Society of Chemistry.
Figure 26 Beam size of the Bruker M6 Jetstream. Reproduced from [19] with permission of The Royal Society of Chemistry.
2.2.2 Synchrotron based instruments

2.2.2.1 DESY
At beamline L of DESY the white radiation emitted from a bending magnet of the second generation synchrotron radiation source DORIS III was employed as primary means of excitation. The Ni/C multilayer monochromator allowed to generate a (1 % ΔE/E) pink beam with an energy between 27 keV and 38.5 keV. In the first experiment at beamline L only a single Ge detector was employed [1]. To record fluorescence radiation from a larger solid angle and so enhance the sensitivity of the instrument in the following experiments, the single detector was replaced with four SD-detectors (see Figure 27). In order to not oversaturate the detectors, the intensity of the beam was adjusted by placing Al absorbers in the beam. The painting was mounted on a motorized stage behind the normal experimental table and moved continuously through the beam for scanning. The beam size was defined by a set of slits placed at the end of the experimental table, which were opened between 0.2x0.25 mm and 1x1 mm (h x v). The beam size was checked to not exceed significantly the pixel size by employing burn paper. The spectrometric figures-of-merit of this scanner operated with a primary beam of 38.5 keV are shown in Figure 19. Results obtained with the DESY scanner and its characteristics were published in [12, 20, 21]. It was also found possible to investigate both sides of a painting simultaneously by placing detectors in front of the painting (facing the beam) and also on the back side [18].

![DESY instrument](image)

*Figure 27 DESY instrument. The beam is coming from the right. The motorized stage is behind the painting and not visible in this picture.*
2.2.2.2 NSLS

Figure 28 Experimental set-up at beamline X7A of the NSLS. Left: “White beam” experiment with a slit system as beam defining optic. Right: Optics of the second experiment: focussing monochromator and bent mirror. With the focussing monochromator no slits were used.

Two experiments were performed at beamline X7A of the NSLS, employing an early 96-element proto type of the Maia detector. In the first experiment the white radiation emitted from a bending magnet of the NSLS was the primary means of excitation. No monochromator was used, but the lower energies, which might heat and damage the painting, were removed from the primary beam by means of a 5-mm-thick Al filter. This filter effectively absorbed all radiation below 20 keV. As beam defining optic a slit system was used.

The acquired data was evaluated with the GeoPIXE software package [22] using off-line dynamic analysis based on the sum spectrum of the entire scan [23]. The elemental distribution images clearly showed the distribution of many elements, but the interference between Hg-L and Pb-L could not be fully resolved under the chosen experimental conditions. This is a result of several factors: (a) the large intensity of the lead fluorescence compared to that of mercury, (b) the lack of a full GeoPIXE model for white-beam excitation and (c) the less than ideal energy resolution of the Maia detector. However, the readability of the Hg-L distribution images could be improved. For this the Pb-L distribution image was multiplied with an correction factor taking the degree of interference between Hg-L and Pb-L radiation into account and subtracted from the acquired Hg-L distribution image [24]. While this procedure enhanced the readability of the Hg-L image, it was still of inferior quality in comparison to elemental distribution images acquired without interference (see section 4.3.1).

Hg is a crucial element in the investigation of historical paintings, as it is present in vermilion (HgS), a red pigment often used in flesh tones. In order to reveal its distribution in the following experiments, monochromatic
radiation was employed. As beamline X7A does not feature a fixed monochromator, a focusing monochromator and bent mirror fabricated from Pt-coated commercial float-glass were installed. As primary energy 12.7 keV were chosen, directly below the Pb-L3 edge, so that the Hg-L3 level was excited, but no Pb-L3 radiation interfered with it in the acquired spectrum. This system allowed to scan paintings with a pixel size of 250 µm.

Characterization and results obtained with this system were previously published in [12, 24].
Figure 29 Sensitivity and Limits of detection normalized to 1 s of the SR based instruments used in this work.
2.3 Comparisons

While it would be desirable to compare the imaging capabilities of all scanners on the same painting, this is not possible for practical reasons. Beam times at SR-sources are commonly only available for the investigation of precious original paintings that only in a few cases could be revisited with a mobile scanner. A notable exception of this was a mock-up study of Rembrandt van Rijn’s *Old Man in Military Costume*. In this study the imaging capabilities of the SR-based DESY and NSLS scanners were compared with that of Instrument A [12]. Beyond that the performance of the Instruments B and D could be compared to that of synchrotron scanners on two paintings by Vincent van Gogh.

2.3.1 Mobile instruments

From instrument A to D an improvement of sensitivity by a factor of 200 can be observed, allowing for the fast acquisition of data with comparable contrast. Instrument A and B are no longer in use, as they offer no advantage over the improved Instruments C and D, and are omitted in this concluding discussion.

The sensitivity of the Instruments C and D and the M6 Jetstream differs considerably. For Zn (Z=30, E(Zn-Kα)=8.6 keV) sensitivity ratios of 1 : 2 : 8.4 (Instruments C : M6 : D) can be observed. Similar values are found for other elements with a fluorescence energy below 20 keV. However, for higher energies the difference increases to 1 : 14 : 135 (Sn, Z=50, E(Sn-Kα)=25.2 keV). This is of importance for the investigation of historical paintings, as Cd (Z=48), Sn (Z=50) and Sb (Z=51), the elements associated with the respective yellow pigments such as cadmium yellow, lead tin yellow and Naples yellow were found crucial in the investigation of several paintings.

There are two reasons for this difference in sensitivity:

1) Beam defining optic: The polycapillary optics used in Instrument C and the M6 attenuate the high energetic part of the primary radiation.

2) Solid angle: The position of the four detectors in Instrument C is not optimal and the single detector of the M6 covers a smaller solid angle than the four detectors of Instrument D.

While these two differences in design give Instrument D a superior sensitivity, they also constitute limitations. The polycapillary lenses used allow to achieve an approximately 15 times better lateral resolution than Instrument D. Furthermore, energy dispersive detectors are among the
most expensive components of an XRF scanner and constitute more than 50% of the total cost for Instrument D.

It is worth noting, that the investigation of historical paintings at maximum resolution is limited to small areas due to the divergence of the primary beams that are focused by polycapillary lenses. In general, paintings are not flat; the paint itself can have a topographic variation of up to several millimetres in height, depending on the painting style. Also, the support may have a curved or undulated surface, making it difficult to keep the distance between the measuring head and the painting within a given tolerance range.

The performance of the three mature XRF scanners (Instrument C, D and the M6 Jetstream) was compared on the same painting: a 20\textsuperscript{th} century copy of an Icon of Saint George (see Figure 30 and Figure 31). For this comparison an overview scan of the whole Icon and a detailed scan of the face of Saint George were recorded. The experimental conditions are given in Table 4. Imperfections in the control software of the M6 Jetstream did not allow for acquisition times in the range of Instrument C and D, while these instruments could not be speeded up to the pace of the M6 Jetstream.

**Table 4 Experimental conditions of scan of St. George Icon.**

<table>
<thead>
<tr>
<th>Overview</th>
<th>Step size [mm]</th>
<th>Dwell time [ms]</th>
<th>Duration [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument C</td>
<td>0.50</td>
<td>175</td>
<td>22.4</td>
</tr>
<tr>
<td>Instrument D</td>
<td>0.50</td>
<td>200</td>
<td>27.7</td>
</tr>
<tr>
<td>M6 Jetstream</td>
<td>0.30</td>
<td>20</td>
<td>6.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Detail</th>
<th>Step size [mm]</th>
<th>Dwell time [ms]</th>
<th>Duration [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument C</td>
<td>0.10</td>
<td>300</td>
<td>25.6</td>
</tr>
<tr>
<td>Instrument D</td>
<td>0.20</td>
<td>250</td>
<td>5.4</td>
</tr>
<tr>
<td>M6 Jetstream</td>
<td>0.05</td>
<td>5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

In Figure 32 the results of the scan of the entire icon is shown. Ca is present in the chalk (CaCO\textsubscript{3}) or gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O) used in the painting’s ground. The Fe distribution is the result of the usage of brownish, reddish earth pigments. The red areas were executed in cadmium red (CdSe), a pigment not used before the 20\textsuperscript{th} century. The elemental distribution images are of comparable quality with the exception of the Cd-K distribution image. Instrument D is giving a clear impression of the Cd distribution, while the other two instruments only produce noisy images. A longer dwell time would improve the quality of the Cd image acquired by M6 Jetstream, but not achieve the same quality as that acquired by Instrument D.
Figure 30 Icon of Saint George, Oil on wood, 20th century.

Figure 31 Detail of Saint George icon.
Figure 32 Results of an overview scan over the Copy of a Saint George Icon. Parameters: See Table 4.
In order to compare the lateral resolution achieved, details of St. George’s face were scanned with a high resolution. While Instrument C and the M6 Jetstream allow to acquire high resolution images, the results acquired with Instrument D seem blurred due to its larger beam size (see Figure 33). The detailed Fe maps acquired with M6 and Instrument C allow visualizing single grains of the paint, when shown in maximal size (see Figure 34).

**Figure 33** Results of a detailed scan over the face of Saint George. Parameters: See Table 4.
Figure 34 High resolution image of the head of Saint George acquired with Instrument C and the M6 Jetstream.
2.3.2 Synchrotron instruments

The two SR-based instruments differed considerably in their nature and performance.

Beamline L of DESY was designed for the investigation of samples with micro-beams, featuring a monochromator permanently installed in the path of the beam that was employed in the experiments to yield primary beams with an energy in the range between 27 and 38.5 keV. Minor rearrangements were necessary to mount the painting on a motorized stage behind the normal experimental table.

Beamline X7A of NSLS is a Diagnostic and Instrumentation beamline for the development of X-ray optics and detectors. No optical elements are permanently installed in the hutch and all components of the scanner needed to be set-up before the experiment. Although, great care was taken to align the components, permanently installed pre-aligned components are expected to make more efficient use of the primary beam’s intensity.

Also the detectors were different. At DESY commercially available SD-detectors with a large active area were used. These detectors allow to cover a large solid angle, but are easily oversaturated. They allow for an energy resolution in the range of 170 eV (calculated as Full-Width-at-Half-Maximum (FWHM) of the Mn-Kα line (5.9 keV)).

At NSLS a 96-element prototype of the Maia detector was used, which was less prone to oversaturation but featured an inferior energy resolution of 320 eV at the Mn-Kα line (5.9 keV). As discussed above, this resulted in difficulties of separating the Hg-L and Pb-L fluorescence radiation in the first white beam experiment, so that in a following experiment monochromatic excitation of 12.7 keV, below the Pb-L3 edge, was employed.

When comparing the spectrometric figures-of-merit in Figure 19, it is obvious that the NSLS instrument with the monochromatic excitation offers the highest sensitivity for elements up to Se (Z=34). In filtered white beam excitation the NSLS instrument is sensitive to a broad range of elements with a maximum for elements around Zr (Z=40).

The DESY scanner operating with primary radiation of 38.5 keV has a comparable sensitivity to the filtered white beam scanner of NSLS, albeit its sensitivity is inferior for elements around Zr (Z=40) but superior for elements heavier than Ag (Z=47, E(Ag-Kα=22.2 keV)).

This can be attributed to the difference in primary radiation. As the primary radiation of DESY is just above the K-edge of Ba (Z=56, E(Ba,K-
(158) Chapter 3 – Data processing

e-edge)=37.4 keV) it is better excited than any of the lighter elements. However, the measured sensitivity for Ba is less than that of, for example, Zr (Z=40) due to the energy dependent detector efficiency (see Figure 14). The shape of the sensitivity curve of the NSLS is different, as here the elements around Zr (Z=40) are more efficiently excited by the white radiation than Ba.

The energy resolution also influences the limits of detection, as a broader peak results in a lower signal-to-noise-ratio (see Eq. 2.8). Thus, the detection limits achieved with the DESY scanner are actually lower than the NSLS scanner employing a filtered white beam, albeit the sensitivity of the latter is higher.

The imaging capabilities of DESY and the monochromatic NSLS scanners were compared in the study of a mock-up of Rembrandt van Rijn’s Old Man in Military Costume from the collection of the Getty Museum (Los Angeles, CA, USA). It is known that under the surface of the original painting a second, overpainted portrait is present, but all attempts to visualize it by imaging techniques such as IRR, XRR or NAAR have failed. It was expected that an investigation of the painting by MA-XRF would reveal additional details of the hidden portrait, which might allow to clarify the position it takes in the young Rembrandt’s oeuvre. In order to identify the instrument best suited for the study of the hidden portrait and identify potential hazards for the original painting during the investigation a full scale, material accurate mock-up of the original painting was created and investigated with three MA-XRF scanners (Instrument A, the DESY scanner and the NSLS scanner). The investigation revealed that both SR-based scanners were capable of visualizing the hidden portrait in the Hg distribution image, while Instrument A was only capable of identifying hot-spots of this element [12]. The elemental distribution maps achieved by both SR-based scanners are shown together with photos of the investigated area in Figure 35.

The NSLS scanner investigated the central area of the mock-up in 5 hours with a lateral resolution of 0.25 mm. The DESY scanner investigated the area in 3 days with a resolution of 0.5 mm. However, it is expected that a reduction of the scan time of the DESY scanner by a factor of 2 or 3 would not interfere with the image quality, behalf that of Ca.
Figure 35 Mock-up of Rembrandt van Rijn’s Old Man in Military Costume. The mock-up was created by painting the hidden portrait (1) and sketching the surface portrait on it (2). The final portrait (3) was subject to this investigation. The area of the face (ca. 25x23 cm) was scanned by the DESY scanner with a step size of 0.5 mm, a dwell time of 1.5 s per pixel for 3 days employing a primary beam of 32 keV. The NSLS scanner employed a dwell time of 18 ms and 0.25 mm step size and scanned the area shown in 5 hours. Adapted from [12] with permission of The Royal Society of Chemistry.
2.3.3 Synchrotron and mobile instruments
In two cases it was possible to directly compare the imaging capabilities of a mobile scanner with that of a SR-based equivalent.

In 2010 Vincent van Gogh’s *Patch of Grass*, which had been subject to previous SR-based investigations [1], was investigated by Instrument B in the Kröller-Müller Museum (Otterlo, NL). Under the surface of *Patch of Grass*, which Vincent van Gogh painted during his stay in Paris in 1887, the study of a female head is present. This was discarded and overpainted by Van Gogh. Details of the face became visible in the Sb (Naples yellow, Pb$_2$Sb$_2$O$_7$) and Hg (vermilion, HgS) elemental distribution images.

In six days, Instrument B was capable of acquiring elemental distribution images of slightly inferior but comparable quality to those acquired with an early SR-based scanner in two days (see Figure 36). Given the difference in sensitivity between Instrument B and D it is expected that Instrument D would allow for the acquisition of a comparable set of images in a single overnight measurement.

The Van Gogh painting *Flower Still Life with Meadow Flowers and Roses*, also from the collection of the Kröller-Müller Museum, was investigated by the DESY scanner and Instrument D. As discussed in detail in Chapter 4, the Flower Still Life was executed on a scene with two half naked wrestlers. At the moment of our investigation of the painting, the authorship of Vincent van Gogh was in general doubted, but it was assumed that a visualization of details in the hidden wrestling scene might provide additional arguments. The painting was scanned from the backside, in order to avoid the absorption of the fluorescence radiation in the thickly painted Flower Still Life. Due to time restrictions, only part of the accessible areas between the stretcher beams were scanned at DESY and additional scans were made with Instrument D, to fill some of the remaining gaps.

While the elemental distribution images of Zn and Hg are of comparable quality, a correct reproduction of the Ba distribution with the mobile instrument was not achieved. All scans were done with a step size of 1 mm and a dwell time between 0.25 and 0.525 s at the synchrotron, while the *in-situ* measurements were done with a dwell time of 3.6 s.
Figure 36 Elemental maps, obtained from Vincent van Gogh’s *Patch of Grass*, showing the hidden portrait of a woman. (a) and (b) show the Sb distribution, while (c) and (d) show the Hg distribution. (a) and (c) were acquired with SR-based MA-XRF, while (b) and (d) are results of in-situ measurements by means of Instrument B. (a) and (c) were acquired with a step size of 0.5 mm and 2 s dwell time in two days, while (b) and (d) were acquired with a step size of 1 mm and a dwell time of 5.1 s in six days. Reproduced from [15] with permission of The Royal Society of Chemistry.
Figure 37 Elemental distribution maps of *Flower Still Life* depicting the hidden painting of the wrestlers. The Zn-K, Ba-K and Hg-L images are superimposed on the X-ray radiograph of the painting. The contour of the two wrestling figures was sketched in to guide the eye. The areas scanned with Instrument D are indicated in the Ba image. Adapted from [18] with kind permission from Springer Science and Business Media.
2.4 Conclusions

In the course of this project considerable progress in terms of instrumentation has been made, but at this moment no ideal instrument that makes all other instruments obsolete is available.

The Maia based scanner at NSLS features a high sensitivity and mature control software that allows acquiring largely noise-free elemental distribution images with just a few milliseconds of dwell time. However, it is limited by its energy resolution and the rather low primary beam intensity at beamline X7A. Howard et al. built an advanced scanner at the Australian Synchrotron, which employed the final 384 element version of the Maia detector and a Kirkpatrick–Baez (KB) mirror pair to yield a beam size of approximately 10x10 µm [13]. In a later experiment the sensitivity of this instrument was found to be approximately double of that of the NSLS scanner’s.

The DESY scanner is limited by its control software, which prevents scans with a dwell time of less than 0.2 s per pixel and due to the monochromatic primary radiation lighter elements are not efficiently excited. However, due to its relatively high sensitivity for K-level radiation of heavy elements such as Ba (Z=56), it constitutes the scanner capable of detecting the broadest range of elements in covered layers.

Notwithstanding their sensitivity, SR-based instruments are limited by the fact that the painting needs to be transported to the synchrotron facility for the investigation, which necessitates considerable logistical and financial efforts. Mobile scanners, that can be used in-situ allow for a much easier investigation of paintings.

Of the mobile instruments presented, the M6 Jetstream is the most versatile scanner, as it allows to acquire high resolution elemental distribution images with reasonable sensitivity. Its main limitations are currently the imperfections in the control software and the lack of sensitivity for X-ray fluorescence lines above 20 keV. The first is expected to be resolved in the near future via software updates. The second limitation might be overcome by installing a collimator optic in front of the X-ray tube and so trade-off lateral resolution for sensitivity.

Instrument C offers no direct advantage over the M6 Jetstream, except being (currently) capable of longer dwell times per pixel. However, its detection geometry can be exploited for depth discrimination (see Chapter 3). Instrument D offers complimentary data to the M6, as it is in general more sensitive, especially to the K-level radiation of heavy elements. It allows visualizing the distribution of elements with better statistics and a
lower noise level than the M6, at a considerably slower pace, due to the limitations of the control software.

To a variable extent, the lack of sensitivity for the K-level radiation of heavy elements is inherent to all mobile instruments. The high energetic primary radiation is strongly scattered in the sample and difficult to shield, so that for radiation protection concerns the maximum energy must be limited.
2.5 References


Chapter 3 - Data processing
## Data processing

### Spectrum evaluation

#### Computing Algorithms

#### Background correction

##### Background estimation

##### Background modelling

### Available software packages

### The in-house written routine – Datamuncher

### Application example

### Conclusions

## Absorption correction

## Depth discrimination

### Test samples

### Angular scans

### Application examples

#### Pauline im weißen Kleid

#### Supper at Emmaus

#### 19th century Russian Icon

### Conclusion

## References
3 Data processing

The requirements on data processing routines for data sets acquired in the investigation of large, heterogeneous, layered samples differ from those for conventional micro-XRF. As such routines were not available in the beginning of this work they were developed in the course of it.

The routines developed fall into three largely unrelated categories and are presented in this chapter in separate sections.

In section 3.1 the development of the Datamuncher software package is described, which employs Dynamic Analysis for the fast processing of large XRF data sets. The section also includes a discussion of different software packages for the evaluation of XRF spectra.

Absorption in covering layers can make elemental distribution images difficult to read. Routines for the removal of such artefacts are presented in section 3.2.

Section 3.3 contains a discussion on how absorption artefacts resulting from covering layers can be exploited to gain additional insights in the stratigraphy of a painting.

3.1 Spectrum evaluation

Scanning XRF investigations aim at the acquisition of elemental distribution images. In these images, the brightness or colour of a pixel is related to the local abundance of an element via the recorded intensity of the fluorescent lines of that element. To achieve this, the characteristic fluorescence lines of the element need to be separated from the other components of the acquired XRF spectrum [1]. This is achieved with dedicated software packages. The software packages used in this work are AXIL [2-4], PyMCA [5] and GeoPIXE [6]. While AXIL and PyMCA were available from the beginning, a GeoPIXE license was not acquired until the last year of this project.

Scanning XRF is commonly used for the investigation of small areas with a limited number of pixels. Often minor or trace level compounds are of interest, requiring dwell times of up to several seconds per pixel. Thus, a software code for the evaluation of a set of XRF spectra acquired under these circumstances does not need to be overly efficient to perform this task in a fraction of the total acquisition time.

However, it is desirable to evaluate data in a timely manner to allow adjusting the schedule or next phase of the experiments on the basis of the results already obtained. In this work, mostly elements present at high concentration levels (often several mass percent) were studied; this
allowed data to be acquired with very short dwell times per pixel (fractions of seconds). Areas of paintings up to several square meters were investigated, so that data sets containing up to several hundred thousand to millions of spectra were acquired. The experiments were commonly done in-situ, so that transfer of the acquired data to a high end multi-CPU PC was rather time consuming; instead software running fast on a mid-level laptop was desired. Under the mentioned circumstances, data processing via AXIL and PyMCA may require several hours, at times taking more time than the recording of the data itself.

As no satisfying software package for fast, in-situ data processing was available, a suitable software package was written in-house, labelled Datamuncher.

In what follows the fundamentals of XRF spectra processing are briefly explained and the available software packages are compared, highlighting their shortcomings that motivated the creation of the Datamuncher. The capabilities of this in-house written software package will be discussed and their value illustrated with selected application examples.

3.1.1 Computing Algorithms
The spectra recorded during scanning XRF experiments consist of partly overlapping characteristic fluorescence lines of the elements present and the spectral background. The latter is a result of scattered primary radiation and incomplete charge collection in the detector(s) employed.

If the escape and sum peaks discussed in Chapter 2 are neglected and the spectral background is assumed to be of constant shape, a spectrum \( S \) can be described by a function \( f \) in channel \( i \) as in Eq. 3.1.

\[
    f_i = a_0 B_i + \sum_{k=1}^{k} a_k y_{i,k} (p_1, p_2, ...)
\]

Eq. 3.1

Where \( B \) is the spectral background. The \( k \) peak profiles \( y \) represent appropriately grouped transitions in the excited atom, such as the radiation resulting from vacancies of the same shell. Their shape is dependent on the non-linear variables \( p \) that contain the energy calibration and resolution of the detector and other characteristics of the spectrometer. The intensity of a peak is expressed in the linear factor \( a \). In elemental distribution images the brightness and colour of a pixel is directly correlated to this factor.

The simplest way to obtain elemental distribution images is to integrate a selected Region-Of-Interest (ROI) of the spectrum around a characteristic line of element \( e \) (see Eq. 3.2).
Chapter 4 – Application Examples

\[ a_e \approx \sum_{i=\text{roi}(1)}^{\text{roi}(0)} S_i \]  \hspace{1cm} \text{Eq. 3.2}

\[ \sum_{i=\text{roi}(0)}^{\text{roi}(1)} a_i y_{i,e} \gg \sum_{i=\text{roi}(0)}^{\text{roi}(1)} B_i + \sum_{k=1}^{k,k\neq e} a_k y_{i,k} \]  \hspace{1cm} \text{Eq. 3.3}

This method provides a good estimate of \( a_i \) in case Eq. 3.3 is valid, i.e. if a high peak-to-background ratio is achieved and no interfering elemental lines are present. Due to the complexity of XRF spectra this is not always the case. The limits of ROI imaging are shown in Figure 38, showing elemental maps obtained by MA-XRF from a painting called ‘Woman with mirror’ by Gerard ter Borch (II) via two data processing methods: the ROI approach and linear least squares fitting (L-LS, see below). The similarity between the Fe images obtained by both data reduction methods suggests that the Fe distribution is correctly determined. This is logical since no interfering elemental lines are present and the Fe signal is considerably more intense than the background throughout the investigated area. Co, however, cannot be clearly separated from Fe, as its Kα line (6.93 keV) interferes with the Kβ line of Fe (7.06 keV). Thus, the Co image obtained via the ROI method strongly resembles the Fe maps while in reality (as better approximated via the L-LS method), the Co distribution is significantly different from that of Fe. Since in XRF spectrometry, quite a few overlaps of this type can occur, in general we can state that ROI imaging is only suitable for preliminary data treatment.

The most common approach of processing XRF spectra is non-linear least squares fitting (NL-LS) to minimize the weighted difference \( \chi^2 \) between the measured spectrum \( S \) and the function \( f \).

\[ \chi^2 = \sum_{i=0}^{i} w_i (S_i - f(a_0, a_1, ..., p_0, p_1, ...))^2 \]  \hspace{1cm} \text{Eq. 3.4}

with the weight \( w_i = \frac{1}{S_i} \) [7].

However, NL-LS is rather time consuming. One approach to render the process faster is to determine all non-linear parameters \( p \) via a non-linear fit of the sum spectrum of the entire data set and to process each individual pixel by linear least squares fitting (L-LS). As already illustrated in Figure 38, L-LS is able to resolve the interferences that are dominating images obtained via ROI integration.
Figure 38  *Woman with mirror*, Gerard ter Borch (II), ca. 1650, Oil on panel, 34.5 x 26 cm² (Rijksmuseum, Amsterdam, SK-A-4039-00). The Fe and Co distributions reveal *pentimenti* around the head of the boy holding the mirror. It is not possible to separate the Co from the Fe distribution by ROI imaging, while linear least square fitting (L-LS) is able to do this. The scan was obtained with the M6 Jetstream MA-XRF instrument with a step size of 0.5 mm and 30 ms dwell time/pixel in 3 hours. The results shown were obtained with PyMCA. This painting was investigated to support the planning of its conservation treatment.

An even faster approach is to perform the least squares fitting operation by a single matrix multiplication. This was proposed by Ryan et al. [8, 9], who called it Dynamic Analysis (DA), as it was primarily meant for online processing during data acquisition.

Their approach it based on the fact that in the multidimensional $\chi^2$ parameter space, at the location of the minimum, the partial derivatives

$$\frac{\partial \chi^2}{\partial a_k} = 0$$

for all parameters $a_k$. This set of conditions leads to Eq. 3.5.

$$\sum_k \sum_i w_i (\partial f_i / \partial a_j) (\partial f_i / \partial a_k) a_k = \sum_i w_i (\partial f_i / \partial a_j) S_i$$

*Eq. 3.5*
This set of simultaneous linear equations can also be expressed as a matrix equation (Eq. 3.6).

$$\alpha a = \beta S$$  \hspace{1cm} \text{Eq. 3.6}

with $$a_{jk} = \sum_i w_i^{-1} \beta_{ji} \beta_{ki}$$ and $$\beta_{ji} = w_i (\hat{c}_f / \hat{a}_j)$$

so the vector $$A$$, which contains all linear intensity factors $$a_k$$, can be calculated as in Eq. 3.7.

$$A = \Gamma S$$  \hspace{1cm} \text{Eq. 3.7}

with the DA matrix $$\Gamma_{ki} = \sum_j \alpha^{-1}_{kj} \beta_{ij}$$.

In case of off-line DA, the matrix $$\Gamma$$ is calculated from the fit of the sum spectrum of a scan. For online DA, which was not employed in this work, it is recommended that the DA matrix is calculated from the NL-LS fit of the sum spectrum of a preliminary scan with reduced lateral resolution. During the calculation of the DA matrix the weight $$w = \frac{1}{f}$$ is employed to avoid introducing errors in spectral ranges of low counting statistics.

DA allows for a much faster data processing and to resolve interferences with results comparable to least squares fitting, as can be seen by comparing Figure 38 with Figure 39. Figure 39 also shows the corresponding 2-element DA matrix in the energy range 6.15-7.25 keV.

![Figure 39 DA matrix for the Fe/Co interference shown in Figure 38, calculated while omitting the spectral background. The results were obtained with the Datamuncher software package.](image-url)
3.1.2 Background correction

In the discussion above we have assumed the spectral background \( B \) in the spectrum to be of constant shape throughout the scanned area. An assumption that is acceptable in many, but not in all cases.

The latter is especially the case for canvas paintings in which in some areas the wooden stretcher is present behind the canvas and in others areas not, resulting in a different background shape due to more and less intense scattered radiation. This is shown in Figure 40, showing part of a large painting entitled *Supper at Emmaus*, controversially attributed to the Italian painter Caravaggio. The stretcher is clearly visible in the image showing the intensity of the spectral background; in the two local sum spectra, the difference in background shape is obvious. The elemental distribution images of Mn and Fe were obtained by DA with GeoPIXE. As the DA matrix assumes the average background shape to be valid in the entire scanned area, above the stretcher the intensity of the fluorescence lines is overcompensated. The extent of this effect is dependent on the signal-to-background ratio. Strong signals, such as Fe in this case, are only weakly affected, while weaker ones, such as Mn, are more strongly perturbed. If the investigated spectral range is limited to a few keV, the shape of the spectral background is more constant and the extent of this artefact reduced. However, taken to the extreme, this would necessitate several fits per data set to cover a large spectral range.

The processes resulting in the measured background are complex, so that no satisfying analytical model to describe it is available. The spectral background can either be estimated and subtracted prior to the fitting of the spectrum or the shape can be included in the model used to fit the spectrum. Modelling the background has the advantage that its shape is “fine-tuned” during the fitting, but also enhances the number of variables that need to be optimized, making the model less stable [2].
Figure 40 Detail of a potential second version of *Supper at Emmaus*, Caravaggio. The difference in spectral background in the region of the stretcher results in visible artefacts in the Mn distribution image. The local sum spectra were obtained on equal sized areas on and off the stretcher indicated by the rectangles in the background intensity image. Data processed with GeoPIXE.
### 3.1.2.1 Background estimation

Different digital filters have been proposed for the estimation of the background in XRF spectra. In the first group, the intensity value of a channel is compared to the mean value of two neighbouring channels (\(w\) channels to the left and right) and if larger, is set to this value, so that after several iterations, the peaks are eroded away (see Eq. 3.8).

\[
y_i = \min\left(\left[y_i, \frac{y_{i-w} + y_{i+w}}{2}\right]\right)
\]

Eq. 3.8

In the most simple case (called the *strip* procedure below) \(w\) is set to 1 and several thousand iterations are needed [10]. In order to achieve a faster processing of data, the Statistical Nonlinear Iterative Peak clipping procedure (SNIP) can be employed [11]. Here \(w\) is initially set to a higher value (typically two times the FWHM of a fluorescence peak are recommended) and stepwise reduced over the iterations until it reaches unity. Instead of several thousand iterations, less than 50 are necessary. These background estimation functions can be easily implemented in the form of digital filters that allow for a fast processing of large data volumes.

The background under a spectrum can also be estimated by fitting orthogonal linear polynomials to the weighted spectral data. By giving more weight to the channels belonging to the background than to those belonging to peaks, the background is estimated in an iterative process. This procedure, called ORTPOL, is only included in the AXIL software package [2].

In spectra with limited statistics, background estimation can result in very low background values, so that no meaningful correction by background estimation is possible.

### 3.1.2.2 Background modelling

The background is in general modelled as either linear or exponential polynomials of degree \(L\), which take the form of Eq. 3.9.

\[
B_i = \sum_{l=0}^{L} (i-i_0)^l \cdot a_l \text{, resp. } B_i = \exp\left(\sum_{l=0}^{L} (i-i_0)^l \cdot p_l\right)
\]

Eq. 3.9

Exponential polynomials are less stable and are not compatible with L-LS, but can adjust better to complex backgrounds shapes than linear polynomials, which are limited to a limited energy range (< 3 keV) or simple background shapes [2].
3.1.3 Available software packages

Table 5 Comparison of XRF software packages

<table>
<thead>
<tr>
<th>Licence</th>
<th>Spectrum processing</th>
<th>Batch processing</th>
<th>Background (spectrum)</th>
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<tbody>
<tr>
<td>LINUX SUSE-AXIL 1.01</td>
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<td>ORTPOL, SNIP, LIN, EXP</td>
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</tr>
<tr>
<td>PyMCA 4.4.0</td>
<td>Open source NL-LS</td>
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<td>Strip, SNIP, LIN, EXP, parabola</td>
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<tr>
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<td>proprietary NL-LS</td>
<td>DA</td>
<td>constant</td>
<td>constant</td>
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</tr>
<tr>
<td>Datamuncher</td>
<td>in-house written None</td>
<td>DA</td>
<td>SNIP</td>
<td>constant, SNIP, LIN</td>
<td>6000 Hz</td>
</tr>
</tbody>
</table>

Abbreviations: LIN: Linear Polynomials, EXP: Exponential Polynomials. *The batch rate of GeoPIXE was determined on a different computer system (see text).

The software packages used in this project are compared in Table 5. The processing speed in spectra per second was measured by processing the data set of Gerard ter Borch’s (II) painting shown in Figure 38, which features 531 x 680 = 361080 pixels. The model contained 17 elemental profiles and 1620 channels in the energy range from 1 to 17 keV. In AXIL and PyMCA a linear polynomial was used as a background model, while the DA based routines used a constant background. AXIL, PyMCA and Datamuncher were run on a small server with eight Intel(R) Core(TM) i7 CPUs 930 @ 2.8 GHz with 12 GB RAM installed operating under Fedora Linux 16. Due to licence restrictions GeoPIXE was run on a laptop with a Intel(R) Core(TM)2 Duo CPU P8400 @ 2.26 GHz with 4 GB RAM operating under 32-bit Windows 7 Professional. A detailed description of the Datamuncher is given in the next section.

The performance of GeoPIXE is correlated to the inferior performance of the computer it was run on. The Datamuncher achieved on the same laptop only a batch rate of 1500 Hz. These numbers illustrate very well that the DA based packages outperform the LS based ones by a factor of approximately 100.

At the beginning of this work, only two software packages were available: (LINUX-)AXIL, which is based on DOS-AXIL, and PyMCA. AXIL was developed at the University of Antwerp since the end of the 1970s. The limited computing resources available during its development necessitated an efficient code, allowing fast least squares fitting of non-linear functions with a broad range of background models on modern computers. In this work only LINUX-AXIL was used.

Limiting factors of (DOS/LINUX)-AXIL are the out-dated Graphical User Interface (GUI) and difficulties to install it on many modern operation
systems without a DOS emulator. Furthermore, AXIL expects every spectrum to be saved as an individual file, necessitating a fraction of a second for data input/output per fit. Also the presence of several ten thousand files in the same folder can slow down the input/output process. The AXIL software package does not include features to create elemental distribution images from the fitted data. This has to be done by external routines.

The software package “microxrf2” by Bart Vekemans (University of Gent, formerly: University of Antwerp) allows to split the data processing with AXIL in parallel processes. In this case the time needed to read the AXIL saved results (.asr) files becomes significant and the processing speed drops from 40 Hz/CPU for a single process to 20 Hz/CPU for six parallel processes.

PyMCA has been developed by the Software Group of the European Synchrotron Radiation Facility (ESRF). It features a modern GUI and is due to its open source character transparent in its inner workings. It includes routines to create elemental distribution images from the fitted data and to export them to common graphic formats. These routines were found sufficient for the first small scans done with Instrument A (ca. 100 x 100 pixels) but were of limited use for the processing of larger scans, e.g. 500 x 500 pixels, so that they were complemented by in-house written software. While its LS routines are not as efficient as that of AXIL (NL-LS was observed at rates of less than 1 spectrum/s/CPU), L-LS data processing is possible at a comparable rate (20 Hz instead of 40 Hz for AXIL). Also PyMCA allows for splitting the data processing into several parallel processes. In this case the pace drops from 20 Hz/CUP for a single process to 10 Hz/CPU for six parallel processes.

In the last year of this project, a licence for GeoPIXE was obtained. GeoPIXE has been developed at the Commonwealth Scientific and Industrial Research Organisation (CSIRO) division of Earth Science and Resource Engineering since the late 1980s. It was to the author’s best knowledge the first software package to include DA and provides a powerful GUI for data processing and evaluation. While originally designed for the processing of data acquired in list-mode (i.e. a list of events with a timestamp, not full spectra per pixel) it was recently expanded towards conventional data formats, including the ESRF data format (.edf), which is also used by the in-house built scanner and PyMCA. The number of computers GeoPIXE can be installed on is limited by its proprietary nature. Another limitation is the assumption of a constant background shape in the calculation of the DA matrix. While in the processing of individual
spectrum, only SNIP is included for background estimation, it is possible to integrate user written plug-ins.

An interesting aspect is also the manner in which the different fluorescence lines of an element are treated. The DA based software packages use during batch processing a fixed intensity ratio of lines per element, separated by shell (K, L or M). AXIL follows the Siegbahn nomenclature (grouping lines by their fluorescence energy) and allows to fit \( K_\alpha \), \( K_\beta \) and \( L_\alpha \), \( L_\beta \) and \( L_\gamma \) lines separately in order to accommodate absorption effects and calculate their ratios after the fitting. While PyMCA allows to fit \( K_\alpha \) and \( K_\beta \) lines, for the L lines the IUPAC nomenclature is used that is well suited for fundamental parameter calculations. So the lines resulting of vacancies in the L1, L2 and L3 shells are treated as one group, modified by absorbers and the detector efficiency included in the model.

3.1.4 The in-house written routine – Datamuncher

In the software packages described above, several features are missing:

- a) In all software packages the start of the fitting process requires user intervention, which prevented efficient use of computing time, e.g. overnight. This is especially hindering, as in the investigation of historical paintings often several data sets of the same painting are acquired, which can be fitted with the same model.
- b) Elements only present locally at a moderate to low concentration level are difficult to identify in a sum spectrum of all spectra of a data set. However, they need to be identified to create a suitable fitting model.
- c) As DA with a fixed background introduced considerable artefacts to the elemental distribution images, a DA routine including variable background shapes was desired.

The development of the Datamuncher was started to solve issue a). The first version automatically generated a list of all data sets in the sub-folders of a directory, calculated sum spectra and started a sequence of batch processes of AXIL and PyMCA. This function is still the core of the Datamuncher software package.

The fit model for the processing of data is in general based on a fit of the sum of all spectra, possibly considering local sum spectra of areas of special interest. However, elements only present locally at a low or medium intensity level can be difficult to distinguish from the summed spectral background (issue b)). The quality of the fit can be checked after the fitting of the data in the distribution image of the summed least square values per pixel, which are an indicator of the quality of the fit. Complex background shapes, as they are typical for X-ray tube based instruments, or artefacts
that are not included in the model (e.g. scatter or diffraction peaks) have a strong influence on the sum of the least squares. In such spectra the contribution of peaks of low or mid level intensity is often not discernible in least squares distribution images.

To identify these minor components in addition to the sum spectrum, a maximum channel spectrum is calculated. In this spectrum the value of each channel is set to the maximum value of this channel in the whole scan data. In this spectrum also elements present in a single pixel at low relative intensity are clearly visible, as can be seen in Figure 41. This solves issue b). Similar routines were previously used in XRDUA [12] and the control software of the M6 Jetstream.

In order to take variable background shapes into account during the processing of a data (issue c)) a DA procedure was implemented in the Datamuncher. For the calculation of the DA matrix, peak profiles obtained from NL-LS fits of the sum spectrum in PyMCA are used. These peak profiles include also the contributions from escape peaks. As with PyMCA a user-friendly and reliable program was available that provided the needed profiles, it was not necessary to write such a routine.

The DA routine of the Datamuncher provides three background modes:

- Constant background. The background shape of the sum spectrum is used for the calculation of the DA matrix.
- SNIP. The background profile is not included in the calculation of the DA matrix. Before the multiplication of the spectrum with the DA matrix the background is estimated and subtracted from the spectrum.
- Linear polynomial. The profile of the background is replaced by a number of profiles representing the terms of the linear polynomial.

As discussed above, the assumption of a constant background is valid in many cases.

Prior to estimation of the continuum via SNIP, the spectrum is treated with a top-hat smoothing filter and is afterwards subjected to the filtering in double logarithmic form. While the simple strip function was found to be too time consuming for practical use, SNIP allows for a good estimation of background shapes if the statistics of the spectrum allows this. However, its iterative nature also slowed down the data processing to ~550 Hz.
Figure 41 Sum spectrum and maximum channel spectrum of a 15th century painting. While in the sum spectrum the small Co and Zn signals can be easily mistaken for tailing of the Fe-Kβ resp. Cu-Kβ radiation, their signals are clearly apparent in the maximum channel spectrum.

Alternatively, linear polynomials can be used. These allow for a faster processing of the data, with only a ~10% loss of pace. However, as discussed above, linear polynomials are best in estimating simple background shapes of limited spectral ranges. As in most cases the SNIP and linear polynomial estimation methods provide comparable results, in general the use of the linear polynomials is favoured.

Beyond the fitting of spectra the Datamuncher package contains routines to correct dwell time variations (as shown in Chapter 2), to stitch of scans of subareas together (shown below) and to create correlation plots of elements (shown in Chapter 4). Beyond these, routines were included to
export the results to common graphic formats (8-bit .PNG and 16-bit .TIF) and to enhance the contrast by limiting the intensity range transformed to the image and by gamma correction.

Currently, the Datamuncher is not taking sum peaks into account. However, algorithms for doing this are included in GeoPIXE [13] and will be integrated in the Datamuncher soon.

3.1.5 Application example
In Figure 42 the painting Supper at Emmaus is shown. While the version of Supper at Emmaus exhibited in the National Gallery in London is accepted to be the autograph version by Caravaggio the status of the painting shown here is controversial. It has been described as a second version created in collaboration by Caravaggio and Prospero Orsi, but this theory is not generally accepted (see [14] and references therein).

In order to find additional arguments in support of or against Caravaggio’s authorship the complete surface of the painting was scanned in 12 sub-areas by means of Instrument D. A step size of 1 mm and an average dwell time of 0.42 s per pixel were employed. The 3.4 megapixel data set, covering an area of 143 x 199.5 cm were acquired in 17 days of scanning, making it the largest area investigated by XRF imaging until now (spring 2013).

The processing of this data set by AXIL employing a single CPU would have required nearly 24 hours of fitting. The parallel use of 6 CPUs would have allowed to finish the processing of the XRF data in 8 hours, not including the time needed for starting the next batch process. With PyMCA the evaluation of this data set would have asked double the time AXIL needed, not considering the fact that due to the lower number of files the data for PyMCA is faster to copy and handle on a computer. The DA routine of the Datamuncher needed less than half an hour to process the spectra with a linear polynomial background model.

The elemental distribution images were corrected for dwell time variations and stitched together to obtain 2037 x 1449 pixel images. The results are shown below. It is worth noting that the artefact induced by the constant background model in Figure 40 was completely corrected in Figure 45. The elements shown are corelated with different pigments. Hg is present in the red pigment vermilion (HgS), which was mainly used in the red clothes but is present throught the painting. Pb is mainly present in lead white (2PbCO₃·Pb(OH)₂). Cu is present in the green and blue pigments that were not only used on their own, but were also added to pigment mixtures to give them a less warm tone. Ca is present as chalk (CaCO₃) and/or gypsum (CaSO₄·2H₂O), used in the ground and fillings of damaged areas. Beyond
that it is also present in bone black. Fe and Mn are both present in earth pigments.

A detailed interpretation of the results obtained and comparison to other works of Caravaggio is still ongoing. However, to the left of the innkeeper an enhanced Pb abundance can be observed. These indicate that the position of the innkeeper has been slightly re-adjusted to the right.
Figure 42 *Supper at Emmaus* (143 x 199.5 cm, oil and tempera on canvas), private collection, as photograph and elemental distribution images of Hg.
Figure 43 *Supper at Emmaus* (143 x 199.5 cm, oil and tempera on canvas), private collection. Elemental distribution image of Pb. The arrows indicate the repositioning of the innkeeper.
Figure 44 *Supper at Emmaus* (143 x 199.5 cm, oil and tempera on canvas), private collection. Elemental distribution images of Ca and Cu.
Figure 45 *Supper at Emmaus* (143 x 199.5 cm, oil and tempera on canvas), private collection. Elemental distribution images of Mn and Fe.
3.1.6 Conclusions

For the investigation of historical paintings a software package is needed that allows for the fast processing of a large number of spectra (several hundred spectra per second) at the site of the experiment and preferably on a mid-range laptop computer.

Different approaches of spectrum evaluation have been considered for this. ROI imaging was found to be fast enough for the task, but as it is not able to properly resolve spectral interferences, it is at best suitable for preliminary data processing. Spectrum evaluation based on (linear or non-linear) least squares fitting, as it is included in the software packages AXIL and PyMCA, is able to resolve these interferences, but was found too slow for in-situ data processing.

Dynamic Analysis (DA) allowed for a fast processing of data and is able to resolve spectral interferences. However, GeoPIXE, which is the only established software package based on DA, became available only late in this work. Also the fixed shape of the spectral background in its DA approach resulted in artefacts if samples with variable X-ray scattering properties were investigated.

The gap in data processing capabilities was filled with an in-house written software package, called the Datamuncher, which allows for fast data processing, also based on DA, with variable background shapes at the site of the experiment. Beyond that the Datamuncher contains features to identify local minor components present in the investigated area and to stitch and export the elemental distribution images acquired.

Next to a fixed background shape two approaches were investigated for background correction: The spectral background can either be estimated by a digital filter (SNIP) and subtracted prior to the evaluation of the spectrum or it can be included in the fit model as a linear polynomial. It was found that in case of historical paintings linear polynomials are sufficient to correct for the spectral background and no artefacts from this approach were observed in the elemental distribution images obtained. SNIP is due to its iterative nature comparably slow, but can correct for background shapes too complex for linear polynomials, provided the individual spectrum of the data set provides sufficient statistics for the application of the filter.

With the exception of the mentioned artefacts largely no difference in the quality of images based on the evaluation with the different software packages was observed. However, if line ratios shift locally due to absorption effects, the LS based packages AXIL and PyMCA are considered to have a slight edge over DA based routines.
3.2 Absorption correction

Artefacts resulting from absorption of fluorescence radiation in covering paint layers can render elemental distribution images difficult to read. Such was the case in the investigation of Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses*, already mentioned in Chapter 1 and discussed in [15, 16] and Chapter 4.

Howard et al. encountered similar problems, when they investigated a self-portrait by Arthur Streeton that had been discarded by the artist and overpainted with a single layer of lead white for reuse [17]. The experiment had been conducted at the X-ray fluorescence microscopy beamline of the Australian Synchrotron employing a Maia detector. In order to avoid the interference between Hg-L and Pb-L fluorescence radiation they chose a primary energy of 12.6 keV, which is below the Pb-L3 edge.

Due to this the distribution of lead white on the surface of the painting could not be directly determined. However, it was found that the intensity of the elastically scattered primary radiation recorded by the detector was proportional to the thickness of the lead white layer, so that they could correct for the absorption in covering layers by means of Eq. 3.10.

\[
I_{corr} = \frac{I_{obs}}{\exp(-\varepsilon S)} \quad \text{Eq. 3.10}
\]

Where \( I_{corr} \) is the intensity corrected for the absorption in the covering lead white layer, \( I_{obs} \) is the recorded intensity, \( \varepsilon \) an empirical factor and \( S \) the intensity of the elastically scattered primary radiation.

However, given the more complex case discussed in this section, no direct correlation between the scattered primary radiation and the absorber thickness was observed, so that more complex correction routines needed to be developed.

The absorption artefacts in Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* are a result of the painting’s complex stratigraphy; this is schematically shown in Figure 46. Starting from the surface, six layers can be discerned: (I) the ‘Flower Still Life’ layer, containing a broad range of pigments in multiple paint layers. It was directly painted in pasteous thick brush strokes without any intermediate ground onto the painting of the wrestling scene (layer II), which in itself consists of multiple pigments and paint layers. The wrestlers were painted on a ground layer (III) that mostly consists of chalk and of which the thickness varies with the weave pattern of the original canvas (layer IV). The original canvas was stabilized by doubling it, i.e. the original canvas was glued on a second canvas (VI). Between the two canvases a layer of
glue (V) is present. Its exact composition and thickness is unknown. On the basis of the Pb-L\textsubscript{\alpha} distribution recorded from the back side such as shown in Figure 47B, we can infer that between the two canvases also a certain amount of lead white is present and that this material is heterogeneously distributed.

As the Flower Still Life (layer 1) was known to be too absorbing to visualize the wrestling scene (layer II) through the top paint layers, the painting was scanned at DESY from the back side, i.e., through the canvas. A primary beam of 38.5 keV was employed. In the area shown in Figure 47, the beam defining slits were opened 0.5 mm, and the scan was executed with 1 mm step size and a dwell time of 0.25 s per pixel. The absorption of the fluorescence radiation emitted from the wrestlers (layer II) in the canvases (layer IV and VI), ground (III) and glue (V) resulted in artefacts in the Zn distribution image shown in Figure 47A. Since zinc white is the main white pigment used to paint the wrestling scene, a correct rendition of the Zn distribution is crucial for the visualization of the covered painting.

**Figure 46** Schematic of layering of Flower Still life. Reproduced from [15] with kind permission from Springer Science and Business Media.

The stripe-like artefacts are the result of absorption of X-rays in the ground layer of the painting that is varying with the weave of the canvas it was applied on. The ground layer is not strongly absorbing as it mostly consists of chalk and organic binders; thus, while elements lighter than Zn (with characteristic energy lower than 8.6 keV) are only weakly detectable, elements with higher fluorescence energies than Zn are much less attenuated by the ground layer and the striping effect is barely discernible. Further, the absorption of the in-homogeneously distributed lead white between the original and superficial paint layers are visible in the form of darker areas in the (Zn) fluorescence maps (see Figure 47AB).

The effect of both artefacts on the final image could be considerably reduced by image processing based on the fundamental parameter approach that is described in [7], by making use of the fundamental
parameters provided by XRAYLIB [18]. In these calculations a simplified model of the irradiated paint multilayer sample was used. Monochromatic radiation of 38.5 keV was assumed to impinge on the sample at $\alpha = 90^\circ$ to the paint surface while the detector was positioned under an angle $\beta$, e.g., $45^\circ$.

The paint layer system was assumed to consist of a layer of pure zinc white (ZnO), covered by a layer of chalk (CaCO$_3$) (layer A) and a layer of lead white [(PbCO$_3$)$_2$·Pb(OH)$_2$] (layer B). Absorption in the organic binders or the canvas material was not taken into account.

In general, the recorded intensity $N_{ijk}$ of line $k$ (e.g., $k = \alpha$ or $\beta$) from shell $j$ (= K in this case) of element $i$ (= Zn) in time interval $t$ is described by Eq. 3.11. This expression was presented in a similar form in Chapter 2.

$$N_{ijk} = t \cdot m_i \cdot Y_{ijk} (E_0) \cdot A_{ijk} (E_0) \cdot A'_{ijk,A} (E_0) \cdot A'_{ijk,B} (E_0)$$  \hspace{1cm} \text{Eq. 3.11}$$

with

$$Y_{ijk} = \frac{\Omega}{4\pi} \cdot \varepsilon(E_{ijk}) \cdot \omega_{ij} \cdot p_{ijk} \cdot I_0(E_0) \cdot \tau_{ij}(E_0)$$  \hspace{1cm} \text{Eq. 3.12}$$

$E_0$ is the energy of the primary beam, $\Omega$ the solid angle within that radiation is recorded by the detector(s), $\varepsilon(E_{ijk})$ is the detector’s efficiency for the energy of the emitted fluorescence energy, $\omega_{ij}$ is the fluorescence yield and $p_{ijk}$ the transition probability of the measured transition. $I_0(E_0)$ is the intensity of the primary beam, $\tau_{ij}(E_0)$ the energy dependent elemental photoelectric cross section, $A_{ijk}(E)$ the self-absorption term (s. Eq. 3.13) and $A'_{ijk}(E)$ an term taking the absorption in the covering layers A and B into account (s. Eq. 3.14).

$$A_{ijk} = \frac{1 - \exp(-\chi_{int}(E_0, E_{ijk}) \rho d_{int})}{\chi_{int}(E_0, E_{ijk}) \rho d_{int}}$$  \hspace{1cm} \text{Eq. 3.13}$$

$$A'_{ijk}(E_0) = \exp(-\chi_{abs}(E_0, E_{ijk}) \rho d_{abs})$$  \hspace{1cm} \text{Eq. 3.14}$$

with
The $\chi(E_0, E_{ijk})$ factor includes the geometrical corrected mass absorption coefficients for primary and fluorescence radiation and $\rho d$ denotes the areal density (product of density and thickness) of the absorbers between the Zn-emitting layer and the detector ($\rho d_{abs}$) and the Zn emitting layer itself ($\rho d_{int}$). $\mu$ is the mass attenuation coefficient.

The first correction makes use of the intensity ratio of the Zn-K\textsubscript{α} (8.63 keV) and Zn-K\textsubscript{β} (9.57 keV) fluorescence lines. Both lines are emitted from an excited Zn atom with a K-level vacancy. When $A_{ijk}$, $A'_{ijk,A}$, $A'_{ijk,B}$ are equal to unity, the ratio between the emitted intensity of the Zn-K\textsubscript{β} and Zn-K\textsubscript{α} lines is 0.1369. Due to absorption along the path towards the detector, this ratio changes, as the Zn-K\textsubscript{α} radiation is (slightly) stronger absorbed than the more energetic Zn-K\textsubscript{β} radiation. The extent to which the Zn signals are attenuated by the paint layer covering the ZnO layer can be used to estimate the areal density of this overlayer on the basis of the observed Zn-K\textsubscript{β}/Zn-K\textsubscript{α} intensity ratio.

\[
\chi(E_0, E_{ijk}) = \mu(E_0) \frac{1}{\sin(\alpha)} + \mu(E_{ijk}) \frac{1}{\sin(\beta)} \quad \text{Eq. 3.15}
\]
Figure 47 Correction of Zn distribution image for absorption effects. A: Zn distribution image, B: Pb distribution image, C: Zn distribution image corrected by using the Zn-K\textsubscript{\beta}/Zn-K\textsubscript{\alpha} ratio, D: Zn distribution corrected by Zn-K\textsubscript{\beta}/Zn-K\textsubscript{\alpha} ratio and Pb correction. Reproduced from [15] with kind permission from Springer Science and Business Media.

Solving Eq. 3.11 for the areal density of the absorbing layer and inserting it in Eq. 3.14 yields:

\[ A'_{ZnK\alpha,A}(E_0) = \left( K_1 \frac{N_{ZnK\alpha}}{N_{ZnK\beta}} \right)^2 \]

where the constants \( K_1 \) and \( K_2 \) are given by:

\[ K_1 = \frac{\varepsilon(E_{ZnK\beta}) \cdot p_{ZnK\beta}}{\varepsilon(E_{ZnK\alpha}) \cdot p_{ZnK\alpha}} \cdot \frac{A_{ZnK\beta}(E_0)}{A_{ZnK\alpha}(E_0)} \]

\[ K_2 = \frac{\sin(\beta)}{\sin(\alpha)} \frac{\mu_{abs}(E_0) + \mu_{abs}(E_{ZnK\alpha})}{\mu_{abs}(E_{ZnK\beta}) - \mu_{abs}(E_{ZnK\alpha})} \]

For the case of a 100 µm thick ZnO layer, for \( K_1 \) a value of 0.167 can be calculated; for respectively a pure chalk or a pure lead white covering layer
a value for \( K_2 \) of -4.0 and -4.7 is obtained. Since neither the thickness nor
the composition of the overlayer is known, the value of \( K_2 \) was empirically
determined. By setting \( K_2 \) to a value of -1.4, noise free images of
considerable increased readability (Figure 47C) are obtained. It should be
duly noted that the applicability of this correction is limited by the statistics
of the measurement since the uncertainty on both the recorded Zn-K\(_\alpha\) and
Zn-K\(_\beta\) intensities propagates into the correction factor. It was found that
this approach yields correction factors leading to adequately artefact-
corrected Zn-maps up to a Zn-K\(_\beta\)/Zn-K\(_\alpha\) ratio of 0.3 (see Figure 47C); this
corresponds to already fairly strong differential absorption. However, since
in the lead white covered areas an even higher ratio was observed, it also
became clear that applying this first correction only was not sufficient to
remove all artefacts from the Zn-image of Figure 47A. Furthermore, it has
to be noted, that as the self-absorption in the ZnO layer is to be assumed
constant in \( K_1 \) a slight loss of contrast occurs.

In order to additionally correct for the shadowing effect on the Zn
distribution caused by (thin layers) of lead white present between the
canvases, a second correction factor was calculated based on the measured
Pb-L\(_\alpha\) intensity.

\[
A'_{ZnKk,B} (E_0) = (1 - \frac{N_{PbL\alpha}}{K_3})^{K_4}
\]

Eq. 3.19

where

\[
K_3 = w_{Pb} \cdot t \cdot \frac{S}{\sin \alpha} \cdot \frac{Y_{PbL\alpha}(E_0)}{\chi_{abs,B}(E_0, E_{PbL\alpha})}
\]

Eq. 3.20

\[
K_4 = \frac{\chi_{abs,B}(E_0, E_{ZnKk})}{\chi_{abs,B}(E_0, E_{PbL\alpha})}
\]

Eq. 3.21

Next to the weight fraction of Pb \( w_{Pb} \) and the area excited by the primary
beam \( S \), other parameters required to calculated \( K_3 \) are the sensitivity for
Pb-L\(_\alpha\) fluorescence radiation \( Y_{PbL\alpha} \) and the primary beam intensity. As with
\( K_2 \), the values of \( K_3 \) and \( K_4 \) were empirically determined by judging the
quality of the final, double corrected Zn-image (Figure 47D). Best results were obtained with a $K_4$-value of 2.7.

By first applying the correction to compensate for the absorption of the Zn-radiation by lead white layer B (with adequately selected $K_4$ value) followed by the correction based on the Zn-$K_{\beta}$/Zn-$K_{\alpha}$ ratio for layer A, the high quality Zn images of Figure 47D could be obtained.

While the calculations described in this section were developed specifically for the data set discussed, they can serve as model for other cases in that complex stratigraphy results in elemental distribution images that are difficult to read due to absorption effects.

(This section was adapted from [15] with kind permission from Springer Science and Business Media.)
3.3 Depth discrimination

In the interpretation of the 2-dimensional projections of an historical painting acquired by MA-XRF, it is often not so much of interest how deep an element is below the surface of the painting, but if it is present in a surface or in sub-surface layer. In the first case, the element is part of the final stage of a painting while in the latter case it often belongs to an intermediate stage or a sketch. Furthermore, it allows gaining insight in the painting technique used during the creation of the artwork.

It is often possible to identify the position of a paint layer in the stratigraphy by comparing the elemental distribution image to the visual impression of the painting, but especially in case of darkened varnish this is not always straightforward.

As discussed in the previous section, the intensity of the recorded fluorescence radiation is dependent on the stratigraphy of the painting as it influences the absorption of X-rays on their path to the detector. The study of thin mono- or multilayers by XRF has been subject to numerous studies in the last decades. While in general, the main focus of these studies was placed on quantitative thickness determination in well characterized systems, several studies on the stratigraphy of paintings have been published.

Already in 1951 the thickness of infinitely thin monolayers of different salts on Mylar film was determined by means of the intensity of the emitted fluorescence radiation [19]. Also the attenuation of a single fluorescence line of the support material was used for the determination of the layer thickness of a covering layer [20] by exploiting equation Eq. 3.14. By employing the ratio of two fluorescence lines resulting from vacancies in the same shell, thickness calculations in multi-layered systems could be performed [21].

An analytical fundamental parameter model describing the fluorescence radiation emitted by thin monolayers and layered samples has been described [22, 23] and experimentally confirmed [24]. Next to the fundamental parameter approach, also Monte Carlos simulation has been used for the study of thin metal films, with largely comparable results [25].

Fiorini et al. described a spectrometer employing a rotation stage that allowed to perform scans over the angle of the incidence of the primary radiation and/or the take-off angle of the emitted radiation [26]. With this instrument, coating thicknesses could be determined. The absorption in covering layers dependent on the detection angle is also exploited in
Grazing-Exit (GE)-XRF, allowing to distinguish between surface and subsurface layers [27].

Kataoka et al. described a wavelength dispersive spectrometer, recording fluorescence radiation of two elements (Fe and Zn) simultaneous at two different exit angles in order to determine the thickness of a Zn coating on steel [28]. Other applications for dual detector instruments have been described by Smilgies et al., who used two detectors to correct for the effect of the relief of Roman inscriptions in marble [29].

Most of these studies focus on homogeneous metal layers, either pure or as alloys. These thickness measurements are of great value for product control, e.g. in case of coated steel or integrated circuits. In these cases also an absolute thickness \( d \) and not only the areal density \( \rho d \) can be determined as the density of metals is well-known and tabulated.

Neelmeijer et al. discussed the problems of depth sensitivity in XRF investigations of historical paintings on a model system of lead white \( \left(\text{PbCO}_3\right)_2\cdot\text{Pb(OH)}_2 \) and vermilion \( \text{HgS} \) double layers and found it of only limited use, compared to PIXE [30]. It was highlighted that the ratio of fluorescence lines of different energy is dependent on the composition of a sample due to (self-) absorption and secondary fluorescence.

Bonizzoni et al. calculated layer thicknesses in Renaissance paintings [31]. For this the pigment(s) present in the surface layer were identified by visible reflectance spectroscopy and the same spot investigated with a well characterized XRF spectrometer. The areal density of a pigment was determined by solving Eq. 3.11 under the assumption of the pigment being the only compound in the surface layer next to the organic binder and the elemental tracer not being present in another layer of the stratigraphy. For covered layers, the transmission of the covering layers for primary and fluorescence radiation was taken into account. They highlighted that for the correct calculation of layer thicknesses in a historical painting it is necessary to know the content of organic binder in a paint layer. The binder is in these calculations a "dark matrix" that cannot be (directly) measured by XRF. Given the simplicity of their model, they consequently conclude that "in some cases, a reliable quantification of ... thicknesses" is possible.

De Viguerie et al. calculated the thickness of paint layers in paintings by Leonardo da Vinci and his student Marco d’Oggiono [32, 33]. The thickness of lead white layers was determined by employing the intensity of the recorded Pb-L radiation and the thickness of layers consisting mostly of organic compounds (glazes and varnish) on the surface of the painting by
employing the Pb-M to Pb-L ratio. By taking the intensity of Ca, Mn and Fe (elements correlated with bone black and earth pigments) into account, a distinction between glazes (containing these pigments) and varnish (not containing them) was found possible. Their analysis relied on detailed knowledge of the paint layers, based on previous studies of the artists’ materials and methods. Based on this knowledge, fundamental parameter calculations were performed with PyMCA. The measurements consisted of line scans and point measurements.

Cesareo et al. were able to determine that a Cu-based pigment was present in the stratigraphy above the lead white dominated layer by comparing the Cu intensity to the Pb-Lα/Pb-\(L_\beta\) ratio [34].

All these calculations are based on Eq. 3.11. Mainly the two absorption effects, i.e., (a) the self-absorption \(A_{ijk}\) in the layer in which the investigated element is present (s. Eq. 3.13) and (b) absorption in covering layers \(A'_{ijk}\) (s. Eq. 3.14) were exploited.

\[
N_{ijk} = t \cdot m_i \cdot Y_{ijk}(E_0) \cdot A_{ijk}(E_0) \cdot A'_{ijk}(E_0)
\]

**Eq. 3.11**

For the self-absorption term, three cases can be distinguished:

(I) Infinite thin sample (small \(\rho d\))

\[
A = \frac{1 - \exp(-\chi_{\text{int}}\rho d_{\text{int}})}{\chi_{\text{int}}\rho d_{\text{int}}} \approx 1
\]

**Eq. 3.22**

(II) Infinite thick sample (large \(\rho d\))

\[
A = \frac{1 - \exp(-\chi_{\text{int}}\rho d_{\text{int}})}{\chi_{\text{int}}\rho d_{\text{int}}} \approx \frac{1}{\chi\rho d}
\]

**Eq. 3.23**

(III) Sample of intermediate thickness

\[
A = \frac{1 - \exp(-\chi_{\text{int}}\rho d_{\text{int}})}{\chi_{\text{int}}\rho d_{\text{int}}}
\]

**Eq. 3.24**

One has to be aware that the mass of element \(i\) \(m_i = w_i \frac{S}{\sin \alpha} \rho d\) contains also the areal density, so that \(N_{ijk}\) in case I is linearly dependent on the areal density, in case II is constant and in case III is non-linearly dependent on the areal density. If all parameters in Eq. 3.11, including the
density $\rho$, are known or can be estimated, the thickness $d$ can be calculated in case I and III.

A layer can be considered infinitely thin if the relative error on the absorption estimation is less than 5% and infinitely thick if the relative error is less than 1%. These values can be calculated by the equations below [35]:

\[
\begin{align*}
    d_{\text{thin}} &\leq 0.1/(\chi_{\text{int}}\rho) \quad \text{Eq. 3.25} \\
    d_{\text{thick}} &\geq 4.61/(\chi_{\text{int}}\rho) \quad \text{Eq. 3.26}
\end{align*}
\]

Mantler et al. calculated under polychromatic excitation with an incident angle of 62.5 degrees and an take-off angle of 45 degrees the absorbance ($1/\chi_{\text{int}}\rho$) for a range of pigments [36]. Based on their results, it was calculated that only in case of high energetic fluorescence radiation such as Cd-K$_a$ (23.1 keV), paint layers can be considered infinitely thin if applied in layers thicker than 3 µm. Pigments with lower energetic fluorescence markers can be considered infinitely thick when applied in layers thicker than 70 µm. These values were calculated for pure pigments with an organic binder that was modelled by water. If these pigments were mixed with pigments featuring heavier elements such as lead white, the intermediate range would be reduced. Nevertheless, most paint layers have to be considered as being of intermediate thickness, even if this is not always possible as will be discussed below.

If not all parameters of Eq. 3.11 are known, the angular and energy dependence of $\chi$ can be exploited (s. Eq. 3.15) and the absorption can be estimated from the ratio of intensities. This allows to remove $Y$ and $m$ from the equation. However, also in this approach either the self-absorption or the absorption in covering paint layers needs to be estimated. As the contribution of the self-absorption is commonly small compared to that of the absorption in the covering paint layers, it is often assumed constant.

If the intensity ratio of two fluorescence lines resulting from vacancies of the same shell is considered, Eq. 3.27 is obtained; this is transformed under the assumption of constant self-absorption to Eq. 3.28 in order to determine the areal density of the absorbing layer. The constant $K_a$ can either be determined experimentally or be calculated based on fundamental parameters and the known characteristics of the instrument.
\[
\frac{N_{ijk}}{N_{ijk+1}} = \frac{\varepsilon(E_{ij}) \cdot p_{ijk}}{\varepsilon(E_{ij+1}) \cdot p_{ijk+1}} \cdot \frac{\exp(-\chi_{abs}(E_0, E_{ij}) \rho d_{abs})}{\exp(-\chi_{abs}(E_0, E_{ij+1}) \rho d_{abs})}
\]
\[
\frac{\chi(E_0, E_{ij}) \rho d_{int}}{\chi(E_0, E_{ij+1}) \rho d_{int}} \cdot \frac{1 - \exp(-\chi_{int}(E_0, E_{ij}) \rho d_{int})}{1 - \exp(-\chi_{int}(E_0, E_{ij+1}) \rho d_{int})}
\]

\[
\rho d_{abs} = (\ln K_a - \ln(\frac{N_{ijk}}{N_{ijk+1}})) \cdot \frac{\sin \beta}{\mu(E_{ij}) - \mu(E_{ij+1})}
\]

Eq. 3.28

with

\[
K_a = \frac{\varepsilon(E_{ij}) \cdot p_{ijk}}{\varepsilon(E_{ij+1}) \cdot p_{ijk+1}} \cdot \frac{A_{ijk}}{A_{ijk+1}}
\]

Eq. 3.29

The dependency of the recorded intensity on the inverse detection angle \(1/\sin \beta\) is expressed in Eq. 3.30. This equation can for the case of two detectors be reformed to Eq. 3.32 that is similar to Eq. 3.28.

\[
\ln N_{ijk} = \ln K_b - \frac{\mu(E_{ij}) \rho d_{abs}}{\sin \beta} + \ln(\frac{1 - \exp(-\chi(E_0, E_{ij}) \rho d_{int})}{\chi(E_0, E_{ij}) \rho d_{int}})
\]

Eq. 3.30

with

\[
K_b = t \cdot m_i \cdot Y_{ij} \cdot \exp\left(-\frac{\mu(E_0) \rho d_{abs}}{\sin \alpha}\right)
\]

Eq. 3.31

\[
\rho d_{abs} = (\ln(K_b') - \ln(\frac{N_{ijk}(\beta')}{N_{ijk}(\beta)}) \cdot \frac{1}{\mu(E_{ij}) \cdot (1/\sin \beta - 1/\sin \beta')}
\]

Eq. 3.32

with

\[
K_{b'} = \frac{A_{ijk}(\beta') \cdot Y_{ij}(\beta)}{A_{ijk}(\beta') \cdot Y_{ij}(\beta')}
\]

Eq. 3.33

While the sensitivity, as it is expressed above, should be independent of the detection angle, in practise the solid angle in which the detectors record fluorescence radiation differs, so that this has to be taken into
account. Similar to $K_a$, the entities $K_b$ and $K'_b$ can be either calculated or experimentally determined. In this work the second approach was followed. Their values were determined from a reference area in experimentally recorded elemental distribution images, so that all absorber areal densities are relative to this position.

**Figure 48 Measurement geometry of Instrument C and the DESY scanner.**

In practice, fluorescence radiation is recorded under four different exit angles (25°, 36°, 39° and 45°) during the measurements with Instrument C and some of the measurements with the DESY scanner (Figure 48). This geometry was chosen as a compromise between a sensitive scanner, which records fluorescence radiation from a large solid angle, and a detection geometry that records fluorescence radiation simultaneously in normal and grazing exit geometry. This compromise was necessary as seldom the opportunity to scan a painting several times is available.

In what follows, linear regression of signals recorded by multiple detectors will be used. As results, images will be shown of which the brightness is correlated to $\mu(E_{ijk})\rho d_{abs}$, so that a bright pixel indicates a covered layer, while a dark pixel indicates a surface layer. These images will be called absorption exponent (abs. exp.) maps. They will be compared to line ratio maps in that the ratio of a higher energetic fluorescence line to one of lesser energy is shown. In the line ratio maps the brightness of a pixel conveys the same information as in an absorption exponent map.
Exploiting the angular dependence of $\chi$ has several advantages over exploiting the energy dependence. The $K_\alpha$ line of an element is commonly $\sim 7$ times as intense as the $K_\beta$ fluorescence line, so that the uncertainty of the ratio of the two lines is dominated by the intensity of the less intense line. In a well-designed instrument, the radiation recorded from different angles will be of comparable intensity. The detection angle can be freely chosen within geometrical limits, while the energy difference between two fluorescence lines is a fundamental parameter. Also performing linear regression with multiple points yields a lower uncertainty than what is achieved in simple ratio calculations with two values.

The disadvantage is that it either requires several scans of the same sample under different detection angles and is thus more time consuming or necessitates the use of multiple (costly) detectors in parallel.

In what follows, both approaches, the exploitation of the angular and the energy dependence of $\chi$, are applied to dedicated test samples and original works of art. This was done to evaluate the possibilities of distinguishing between surface and covered paint layers by dedicated data treatment.

In view of the limited statistics, no quantification of the absorber thickness was attempted and the areal densities were only compared qualitatively. A full quantification is also not possible, as the mathematical model employed is too simple for the rather complex systems and would necessitate detailed knowledge on the materials used, also in sub-surface layers, including the amount of the organic binder present.
3.3.1 Test samples

Figure 49 Test samples: A (upper row) cadmium yellow; B (lower row) lead white of different nominal thickness (20, 50, 100, 200 µm). Al absorber foils of different thicknesses, nominally 15, 30 and 60 µm in thickness, were placed on top of both rows (only shown on A here). Samples were made by G. Van der Snickt.

Two test samples were prepared, employing commercially prepared cadmium yellow and lead white (see Figure 49). In the cadmium yellow, next to the main colouring component (CdS), Zn and Ba were found to be present at a concentration level of several mass percent (estimated from the acquired XRF spectrum of the paint and the known sensitivity of Instrument C given in Chapter 2). These are probably present in the form of extenders such as zinc oxide (ZnO) and barium sulfate (BaSO₄).

The paint was applied on 2 mm thick polycarbonate plates in four squares of 20 µm, 50 µm, 100 µm and 200 µm thickness with a Zehnter ZUA 2000 Universal Applikator. As absorber, commercial Al foil with a nominal thickness of 15 µm was used to achieve homogeneous, reproducible absorption of the fluorescence radiation emitted by the samples. By means of a Vernier calliper the thickness of the Al foil was confirmed to be less than 17 µm. Next to Al, a low concentration of Fe (~5-10 m%, estimated from the absorption of X-rays in the foil) was found to be present in the Al foil.

The paint was covered with a single layer (15 µm), a double layer (30 µm) and four layers (60 µm) of Al foil. Below the Pb-L3 edge (13.0 keV) these
Al layers are roughly 20% as absorbing as a lead white layer (80% pigment, 20% binder) of equal thickness. However, above the Ca-K edge (4.0 keV), the absorption is comparable to that of a gypsum layer (60% gypsum, 40% organic binder) of equal thickness. The modelling of weakly absorbing layers was deliberate, as the distinction between surface and thinly covered sub-surface layers is in such cases especially problematic. The results obtained on both samples with instrument C are shown in Figure 50.

![Elemental distribution images](image)

**Figure 50** Elemental distribution images obtained from test samples A (cadmium yellow) and B (lead white) with Instrument C operated at 50 kV, 1 mA, a step size of 0.5 mm and a dwell time of 2.9 s. Results shown were obtained with PyMCA on the summed spectra of all detectors. A brighter colour corresponds to a higher abundance of the element.

In sample A, Zn is well detectable through all absorbing Al layers, which, as mentioned above, contain a small amount of Fe. The Cd-K fluorescence radiation is weakly and the Ba-K radiation barely detectable due to the limited sensitivity of Instrument C for these elements. For both elements no absorption in the covering layers can be observed. The L-level fluorescence radiation of both elements is well detectable, but while the Cd-L radiation is only detectable if no absorbing layer is present, the Ba-L radiation is well detectable through one layer of Al and barely through two
layers. In case of sample B, the L-level radiation of Pb is detectable through all layers, while Pb-M is only detectable if no absorber is present. **Figure 51** Depth discrimination in test samples A and B. In all maps the brightness of a pixel is proportional to the absorption in covering layers. In case of sample B, the Pb-L lines were used, while in sample A the Zn-K lines were employed. Pixels featuring a low signal of the element in question were set to 0. The greyscale of the line ratio images was chosen so that the image obtained is not dominated by extreme values. Numerical values for the different paint and absorber thicknesses are given in Table 2ab and Table 3ab.

In Figure 51 the line ratio and absorption exponent maps of sample A and B are shown. Both samples were investigated with a dwell time of 2.9 s per pixel, which is rather long compared to scans done in-situ. The scan of sample A was repeated with a dwell time of 0.2 s to apply both methods of depth discrimination under less favourable conditions. Line ratios were calculated for the most intense lines of the elements Zn and Pb. The Zn-K_α (8.63 keV) and Zn-K_β (9.57 keV) lines were used for Zn; for Pb, the lines resulting from vacancies in the Pb-L_3 (strongest transition: L_3M_5 (10.55 keV)) and the Pb-L_2 (strongest transition: L_2M_4 (12.61 keV)) shell were employed.

The maps obtained by both methods in the measurements with 2.9 s dwell time allow to clearly distinguish between different degrees of absorption.

Furthermore, it is obvious that minor folds in the Al foil are visible in the absorption exponent map, as opposed to the line ratio map. These folds result in variation of the effective absorber thickness dependent on the detection angle, so that their effect on the absorption exponent map is
large. For the line ratio map the effect is largely averaged out when the spectra of the four detectors are summed up for the processing in PyMCA.

If the dwell time per pixel is reduced from 2.9 s to 0.2 s with otherwise identical parameters, the different absorber thicknesses are much more apparent in case of the absorption exponent map. This is due to the low intensity of the Zn-Kβ line compared to the Zn-Kα line, which dominates the uncertainty of the calculated areal density of the absorber.

The ratios of the averaged line intensities for all combinations of layer and absorber thickness of sample A and B are shown in Table 2ab and Table 3ab. The nominal thickness of the Al foil (assumed to be 93 m% Al and 7 m% Fe) can be correctly calculated by Eq. 3.28, with the constant $K_\alpha$ calculated from the 100 µm thick, surface paint. With the exception of the 20 µm thick paint layer of test sample A, the layer thickness is well estimated and allows for a reliable distinction between surface and sub-surface layers. The overestimation of the Al foil thickness in case of the 20 µm paint layer of sample A is attributed to the overestimation of the Zn-Kβ intensity in spectra with a low signal-to-background ratio.

In case of sample B, a systematic overestimation of the 60 µm Al absorber can be observed. This is attributed to the fact that the recorded Pb XRF intensities are not emitted from the same shell. With increasing Al thickness, fewer vacancies are created in the Pb-L3 level than in the Pb-L2 level. However, the absorption of the primary radiation only has a small influence on the observed line ratio compared to the absorption of the fluorescence radiation.

Table 3ab the results for the angular dependent determination of the layer thickness are given. The sensitivity factors were determined from the 100 µm thick paint layer without absorber. A clear distinction between covered and surface paint layers is possible and the layer thickness is largely calculated correctly. However, in sample A, a clear distinction between the 200 µm thick surface layer and the 20 µm thick paint layer covered with 15 µm of Al based on a single measurement might prove difficult.

For both approaches a considerable contribution of the self-absorption to the calculated layer thickness can be observed. This effect seems to be stronger for angular dependent measurements than for the comparison of fluorescence lines of different energies.
### Table 6a Line ratios of Zn-K\(_{\beta}/Zn-K\alpha\) in test sample A and calculated layer thickness.

<table>
<thead>
<tr>
<th>Sample A - Zn-K(_{\beta}/Zn-K\alpha) ratio</th>
<th>Nominal Thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>0.182</td>
<td>0.179</td>
<td>0.182</td>
<td>0.184</td>
<td></td>
</tr>
<tr>
<td>15 µm Al</td>
<td>0.207</td>
<td>0.204</td>
<td>0.202</td>
<td>0.203</td>
<td></td>
</tr>
<tr>
<td>30 µm Al</td>
<td>0.231</td>
<td>0.219</td>
<td>0.218</td>
<td>0.202</td>
<td></td>
</tr>
<tr>
<td>60 µm Al</td>
<td>0.319</td>
<td>0.269</td>
<td>0.259</td>
<td>0.267</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated layer thickness</th>
<th>Nominal Thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>0.0</td>
<td>-2.4</td>
<td>0.0</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>15 µm Al</td>
<td>19.3</td>
<td>17.3</td>
<td>15.4</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td>30 µm Al</td>
<td>35.4</td>
<td>27.8</td>
<td>26.5</td>
<td>28.3</td>
<td></td>
</tr>
<tr>
<td>60 µm Al</td>
<td>82.8</td>
<td>57.9</td>
<td>52.4</td>
<td>56.7</td>
<td></td>
</tr>
</tbody>
</table>

### Table 6b Line ratios of Pb-L\(_2/L\_3\) in test sample B and calculated layer thickness.

<table>
<thead>
<tr>
<th>Sample B - Pb-L(_2/Pb-L_3) ratio</th>
<th>Nominal thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>0.364</td>
<td>0.378</td>
<td>0.397</td>
<td>0.405</td>
<td></td>
</tr>
<tr>
<td>15 µm Al</td>
<td>0.423</td>
<td>0.429</td>
<td>0.446</td>
<td>0.455</td>
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</tr>
<tr>
<td>30 µm Al</td>
<td>0.481</td>
<td>0.479</td>
<td>0.497</td>
<td>0.504</td>
<td></td>
</tr>
<tr>
<td>60 µm Al</td>
<td>0.593</td>
<td>0.585</td>
<td>0.609</td>
<td>0.618</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated layer thickness</th>
<th>Nominal thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>-14.6</td>
<td>-8.4</td>
<td>0.0</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>15 µm Al</td>
<td>10.5</td>
<td>12.5</td>
<td>19.2</td>
<td>22.4</td>
<td></td>
</tr>
<tr>
<td>30 µm Al</td>
<td>31.4</td>
<td>30.8</td>
<td>37.1</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>60 µm Al</td>
<td>66.2</td>
<td>64.1</td>
<td>70.5</td>
<td>73.1</td>
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</tr>
</tbody>
</table>
### Table 7a Calculation of layer thickness of test sample A based on multi-angular measurements.

Sample A – Absorption exponent calculated for Zn

<table>
<thead>
<tr>
<th>Nominal thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm Paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>-0.148</td>
<td>-0.094</td>
<td>0.001</td>
<td>0.040</td>
</tr>
<tr>
<td>15 µm Al</td>
<td>0.087</td>
<td>0.129</td>
<td>0.175</td>
<td>0.299</td>
</tr>
<tr>
<td>30 µm Al</td>
<td>0.385</td>
<td>0.456</td>
<td>0.533</td>
<td>0.639</td>
</tr>
<tr>
<td>60 µm Al</td>
<td>0.695</td>
<td>0.952</td>
<td>1.074</td>
<td>1.020</td>
</tr>
</tbody>
</table>

Calculated layer thickness

<table>
<thead>
<tr>
<th>Nominal thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm Paint</th>
<th>200 µm Paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>-9.8</td>
<td>-6.2</td>
<td>0.1</td>
<td>2.7</td>
</tr>
<tr>
<td>15 µm Al</td>
<td>5.8</td>
<td>8.5</td>
<td>11.5</td>
<td>19.7</td>
</tr>
<tr>
<td>30 µm Al</td>
<td>25.4</td>
<td>30.1</td>
<td>35.2</td>
<td>42.2</td>
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<tr>
<td>60 µm Al</td>
<td>45.9</td>
<td>62.8</td>
<td>70.9</td>
<td>67.4</td>
</tr>
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</table>

### Table 7b Calculation of layer thickness of test sample B based on multi-angular measurements.

Sample B – Absorption exponent calculated for Pb

<table>
<thead>
<tr>
<th>Nominal thickness</th>
<th>20 µm paint</th>
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<th>200 µm paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 µm Al</td>
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<tr>
<td>15 µm Al</td>
<td>0.102</td>
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</tr>
<tr>
<td>30 µm Al</td>
<td>0.288</td>
<td>0.321</td>
<td>0.338</td>
<td>0.307</td>
</tr>
<tr>
<td>60 µm Al</td>
<td>0.536</td>
<td>0.575</td>
<td>0.614</td>
<td>0.494</td>
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</table>

Calculated layer thickness

<table>
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<tr>
<th>Nominal thickness</th>
<th>20 µm paint</th>
<th>50 µm paint</th>
<th>100 µm paint</th>
<th>200 µm paint</th>
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</thead>
<tbody>
<tr>
<td>0 µm Al</td>
<td>-10.6</td>
<td>-6.3</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>15 µm Al</td>
<td>11.5</td>
<td>7.4</td>
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<tr>
<td>30 µm Al</td>
<td>32.4</td>
<td>36.1</td>
<td>38.0</td>
<td>34.5</td>
</tr>
<tr>
<td>60 µm Al</td>
<td>60.2</td>
<td>64.7</td>
<td>69.1</td>
<td>55.6</td>
</tr>
</tbody>
</table>
3.3.2 Angular scans

It would be desirable to distinguish between the contributions from self-absorption and absorption in covering layers. To explore the possibility to do so in multi-angular measurements, components of Instrument D were rearranged in a geometry similar to that described by Fiorini et al. [26].

X-ray tube and sample were mounted on an optical rail, with the collimated beam impinging on the sample at 45°. Two detectors were mounted on a rotation stage (Micro-controle spectra-physics S.A, Évry, France) with the centre of rotation positioned below the interaction volume of beam and sample (see Figure 52). Only the signals recorded by the detector facing the paint were evaluated.

Curves recorded of a 100 μm thick lead white layer without absorber and covered with 15 μm and 30 μm of Al foil are shown in Figure 52. These curves were fitted to Eq. 3.34.

\[
R = \left( \frac{K_1}{1 / \sin \beta + K_0} + K_2 \right) \cdot \exp \left( \frac{K_3}{\sin \beta} \right) \quad \text{Eq. 3.34}
\]

with

\[
K_0 = \frac{\mu_{\text{int}}(E_0)}{\mu_{\text{int}}(E_{ijk}) \cdot \sin \alpha} \quad \text{Eq. 3.35}
\]

\[
K_1 = t \cdot m_i \cdot Y_{ijk} \cdot \exp \left( -\frac{\mu(E_0)_{\text{abs}} \rho d_{\text{abs}}}{\sin \alpha} \right) \cdot \frac{1}{\mu(E_{ijk})_{\text{int}} \rho d_{\text{int}}} \quad \text{Eq. 3.36}
\]

\[
K_2 = -\mu(E_{ijk})_{\text{abs}} \rho d_{\text{abs}} \quad \text{Eq. 3.37}
\]

\(K_2\) is an empirical parameter that was found to be necessary to properly fit the curves. It is used to describe effects such as secondary fluorescence and scattering. While a good representation of these curves were obtained, it was not possible to separate in a reliable fashion the contributions of self-absorption and absorption in the covering layers.

This can be partly attributed to minor deviations from the assumed measurement geometry as well as to limitations of the model used. However, the conditions to properly distinguish between self-absorption and external absorption were considerably more favourable in this experiment than in the data acquired by Instrument C. Consequently, no attempt was made to distinguish between the two forms of absorption.
during data processing of imaging, but it was taken into account during the interpretation of the obtained maps.

Figure 52 Experimental set-up to scan the angle of detection as photography and schematic drawing. Below: Curves obtained on 100 µm paint with 15 µm and 30 µm Al absorbers. Dashed lines indicate the angles from which fluorescence radiation is recorded by instrument C. The detection angle was varied in steps of 0.5° with a dwell time of 10 s per step. The X-ray tube was operated at 45 kV and 0.2 mA.
3.3.3 Application examples

3.3.3.1 Pauline im weißen Kleid
In Figure 53 the painting *Pauline im weißen Kleid vor sommerlicher Baumlandschaft* is shown. The painting is controversially attributed to Philipp Otto Runge and a full discussion of this case study is presented in Chapter 4. The distribution of Hg results from the use of the red pigment vermilion (HgS). When the Hg-L distribution image is compared to the photograph of the painting, it becomes clear that in an earlier version the sitter was depicted with bands in her long(er) and open hair. These bands have been overpainted to create the current, more modest impression. The originally brighter (but not necessarily blonde) hair is well discernible in the Sb distribution image, which is assumed to be present in the pigment Naples yellow (Pb$_2$Sb$_2$O$_7$).

The painting was investigated at DESY. To determine the line ratios of different elements, the spectra of all four detectors were summed and evaluated with AXIL. For the multi-angular calculations, the spectra of the individual detectors were processed with the DA routine of the Datamuncher.

In the interpretation of the line ratio images, it is important to be aware of a special absorption effect: the Pb-L$_\beta$ (12.6 keV) radiation is above the Hg-L3 edge (12.3 keV), so that if a vermilion layer is present directly above a lead white layer, the Pb-L$_\beta$ is weakened and the Hg-L$_\alpha$ enhanced. Thus, for both elements the L$_\beta$/L$_\alpha$ ratio drops, which is commonly used as an indicator of the position of these elements closer to the surface. This effect is long known [30].

Lead white is present in the ground layer throughout the painting and in the pictorial layers. In the Pb-L$_\beta$/L$_\alpha$ ratio image, horizontal strokes can be observed that result from in-homogeneities in the thickness of the ground layer. (The slight vertical lines are the result of injections of new positrons into the storage ring during the experiment.) The hair bands of the sitter are visible as dark areas, which can be mistaken as an indicator for the presence of Pb close to the surface. However, it is the result of the selective absorption of the Pb-L$_\beta$ radiation by the vermilion discussed above.

This is not apparent in the absorption exponent image, in which the covered hair bands are, as expected, shown as bright areas, indicative of the presence of strongly absorbing covering layers. Beyond this, the image features also slight artefacts from ring injections that were not completely corrected for. The effect of the varying ground thickness is less apparent than in the line ratio image, but the surface topography has an influence on
the image. The small features correspond at least partly to cracks in the painting. For the multi-angular calculations, the Pb-L signals were normalized to the average intensity of the entire scanned area.

When the belt of the final portrait is compared with the Hg-L distribution image, it is obvious that its position has been slightly adjusted. The later added upper right part of the belt (red square in Figure 16) was used to determine $K_b$ for the calculation of the absorption exponent map (see Eq. 3.30). In the Hg-L$_\beta$/L$_\alpha$ image, this area is correctly identified as a surface area. Also the hair bands are correctly identified as being covered, with the notable exception of those in the upper right corner (yellow arrow). This can be attributed to enhancement of the Hg-L$_\alpha$ radiation due to the selective absorption effect described above and by the presence of a covering layer that absorbs less in this area than above the other hair bands. The same observations can be made for the absorption exponent image.

No information on the stratigraphy of the face could be obtained, as no strong effects were observed and Hg is present in a mixture with other elements, making an estimation of the self-absorption difficult. Also the stratigraphy of the belt could not be fully resolved; it was only possible to observe that the straightened belt was painted on a more curved one.
Figure 53 Detail of *Pauline im weißen Kleid vor sommerlicher Baumlandschaft*, controversially attributed to Philipp Otto Runge. The Sb image reveals the original hair style of the sitter and the Hg distribution image shows the presence of red bands in her hair. In line ratio and absorption exponent maps the brightness of a pixel is proportional to the absorption in covering layers. Both confirm the presence of most, but not all, overpainted features below the surface.
3.3.3.2 Supper at Emmaus

Figure 54 Detail of *Supper at Emmaus*. Results were acquired by means of Instrument C (50 kV, 1 mA, 0.5 mm steps, 0.75 s/pixel.)
An interesting area of the painting *Supper at Emmaus* (mentioned in section 3.1.5) is that of the half shadowed wine leaf on the table next to the fruit basket (s. Figure 54). One might expect the wine leaf to have been painted as a whole and the shadow (right half of the leaf) to have been added later by superimposition of a dark transparent layer or glaze. While this assumption at first appears to be confirmed by the more or less homogeneous Cu distribution and the high abundance of Fe and Ca in the shadowed part, the distribution of Pb contradicts this. The XRR also reveals the dark half of the leaf to be less absorbent than the bright part. In the left half of the leaf, both Pb (from lead white) and Cu (from Cu-based pigments) are present while in the right half, Cu-based pigments may have been mixed with earth pigments to obtain a darker tone of green. We conclude that the brightened and shadowed halves of the leaf were executed separately. However, the application of a thin glaze layer on the shadowed part cannot be excluded. The veins, on the other hand, were probably executed later using a lighter tone of green (i.e., with paint richer in lead white) (adapted from [37]). The Pb-L and Pb-M images illustrate the different information obtained from both Pb lines. While in the Pb-L distribution image, contributions from the ground following the canvas weave pattern are visible, the Pb-M image is dominated by the lead that is present at the surface of the painting.

In order to obtain easily readable line ratio maps, superpixels consisting of the sum of 4x4 pixels, were calculated, yielding a data set of better statistics but inferior lateral resolution. The results of both depth discrimination approaches agree well with each other, but provide rather counter-intuitive results (see Figure 55). The bright side of the leaf is seemingly covered by a thicker absorber than the shadowed side. However, superimposing bright paint layers on a darker one to lighten the area would be a rather unusual painting technique.

Also the dark grapes to the right of the leaf are indicated to be present at the surface of the painting. A paint cross-section taken from the dark grapes was prepared and investigated by SEM-EDX. This revealed that the Cu is present in the second layer under the surface and covered by a thin (~15-30 µm) earth pigment layer, while Pb is homogeneously distributed through the surface layers. It can be assumed that the dark grapes were created by superimposing a layer containing a dark earth pigment and black carbon on a green Cu pigment based layer. The latter is still slightly shining through the covering layer, contributing to the visual impression. The green grapes are assumed to be executed in a mixture of lead white and Cu-based green, which is probably present at the surface of the painting. However, also in case of the green grapes a thicker covering layer than the dark grapes is indicated by both depth discrimination approaches.
The results found in this case are counter-intuitive and can be easily misinterpreted. This is assumed to be caused by the difference of self-absorption in layers where green Cu pigments are present mixed with lead white and those where they are present without it.

Figure 55 Top: Absorption exponent and line ratio maps. In both the brightness of a pixel is proportional to the absorption in covering layers. The Cu-\(K_β/K_α\) ratio was calculated on super pixel created by adding up 4 x 4 pixels. As reference area for the angular dependence the shaded part of the wine leaf was used (indicated by red shape). Bottom: SEM-EDX images of a polished paint cross section. The location of the sampling is indicated by the red cross in the absorption exponent map. The paint cross section was prepared and investigated by G. Van der Snickt.
3.3.3.3 19th century Russian Icon

In Figure 56 an Icon in Russian style is shown. The history of the object is largely unknown, but it is assumed to be created in Russia in the 19th century. The pigments employed to create the icon were found to be Au, earth pigments (Fe and Mn), green and yellow Cr-based pigments (chrome oxide greens and chromates), vermilion (HgS) and lead white (2PbCO$_3$·Pb(OH)$_2$). These are pigments typical for the 19th century.

The Au was applied in two steps. Before the execution of the painting, thin Au leafs were applied on the ground layer and overpainted. This is the case for the halos of the saints and the incense burner. The strong reflection of visible light still contributes to the visual impression of the painting because the Au leafs are only thinly covered in many areas. However, often the Au was also left exposed deliberately. After the execution of the other paint layers, Au accents were applied to the surface, e.g. in the clothes of the saints. This was probably done with Au paint that consists of Au powder dissolved in a water soluble binder [38]. In some areas, especially the faces of the saints, paint losses occurred, exposing the Au leafs.

In the context of determining the painting’s stratigraphy by comparing the absorption of the emitted fluorescence radiation, the partially overlapping Au leafs are very suitable samples. Due to the quasi-uniform thickness, the self absorption in the Au leafs is approximately constant and the fluorescence radiation emitted by them is of sufficient energy to penetrate the covering layers.

To investigate the position of Au in the stratigraphy of the painting, several depth profiles were acquired by means of confocal XRF. The experiments were done at C2RMF (Centre de Recherche et de Restauration des Musées de France) in Paris (FR), making use of the LouX$^{3D}$ instrument [39]. The instrument features a depth resolution of approximately 50 µm for Zn-K$_\alpha$ (8.6 keV) fluorescence radiation, which gradually improves with rising energy. Selected depth profiles obtained are shown in Figure 57. It is obvious that at locations 2 and 3, Au is present at the surface of the painting, while in case of points 1 and 4, it is covered by paint layers. It is worth noticing that the Au depth profiles are in general Gaussian shaped, indicating the presence of Au in a single, thin layer much smaller than the sampling depth of the confocal setup. In point 2, however, the profile diverges from this shape, indicating that Au is present in two superimposed layers that cannot be completely resolved by confocal XRF with this instrument.
Figure 56 19th century Russian Icon, private collection. The area shown (16 x 18.5 cm) was investigated by means of Instrument C with a step size of 0.25 mm a dwell time of 0.42 s. The X-ray tube was operated at 50 kV and 1 mA.
Figure 57 Depth profiles obtained at four locations of the icon. Step size was in all scans 5 µm and dwell time varied between 30 s (point 4), 50 s (point 1 and 3) and 100 s (point 2). The X-ray tube was operated at 50 kV and 0.6 mA.
Depth discrimination techniques applied to the Russian Icon. On the left (absorption exponent and line ratio maps) a brighter colour indicates a thicker absorber. On the right, the Au-L3 distribution image is re-coloured, indicating surface (red) and covered (green) paint layers. The threshold between the two was selected based on the stratigraphy known from the confocal XRF measurements. Yellow arrows indicate areas where the two depth discrimination techniques are not in agreement, blue arrows indicate areas where Au paint is present on top of Au leaf (see text).

The results of the depth discrimination techniques are shown in Figure 58. For the multi-angular measurements, the area indicated by the yellow square was used as a reference area. The results are in good agreement and correctly allow distinguishing between surface and covered layers. However, in some areas covered paint layers are detected with the line ratio method and not by the multi-angular measurement (yellow arrows in Figure 58). These are areas in which also large amounts of Hg are present.
in the form of the red pigment vermilion (compare to Figure 56). As the Au-L$_\beta$ (11.44 keV) and Hg-L$_\beta$ (11.82 keV) fluorescence lines partly overlap and cannot be fully separated, the Au-L$_\beta$ intensity is slightly overestimated here and the corresponding region is incorrectly identified as being covered.

In a few areas, Au paint is present on top of the Au leafs, so that Au is present in a double layer, separated by layers of other pigments. In this case not all pixels are attributed to the surface and a region with less clear attribution is obtained.

3.3.4 Conclusion

Two methods to discriminate between the surface and sub-surface layers of paintings in elemental distribution images acquired by MA-XRF have been explored. These methods are based on exploiting the energy or detection angle dependent absorption of fluorescence radiation in covering layers. No quantitative determination of the layer thicknesses was attempted and the results obtained were always relative to a reference point in the scanned area.

The uncertainty of the K$_\beta$ and K$_\alpha$ ratio is determined by the statistics of the less intense K$_\beta$-radiation. Here the multi-angular method has the advantage that fluorescence lines of roughly equal intensities are compared. This was shown in the study of *Supper at Emmaus*, where the fluorescence radiation of Cu was investigated. To obtain easily readable results, superpixels had to be created by adding up the spectra of 4 x 4 pixels.

In case the intensity of transitions resulting from vacancies in the L2 and L3 shell are compared, the statistical edge of the multi-angular method is of less importance as these lines are of comparable intensity. However, the multi-angular method is less influenced by spectral interferences and absorption processes that change the line ratio.

The advantages of the angular dependent approach none withstanding, it also puts higher demands on the MA-XRF scanner that needs to be equipped with at least two XRF detectors with different detection angles. The efficiency of the angular dependence based approach could be enhanced if the difference in detection angle would be maximized. Such an instrument might employ one detector at a (nearly) normal angle to the painting surface and a second in (nearly) grazing-exit geometry.

In both methods a considerable influence of the self-absorption on the results was observed. Attempts of separating the contributions of both absorption processes in the data processing were not successful. In test
samples and application examples, it was found that the self-absorption cannot be neglected and is strongly dependent on the paint layer composition, as well as on the layer thickness. The results obtained on the test samples suggest that angular dependent measurements are more sensitive to self absorption and to in-homogeneities in the layer thickness, such as the folds in the Al foil. This could also be observed in the case study on *Pauline im weißen Kleid*, where cracks in the painting’s surface were clearly visible in the absorption exponent map. The obtained maps of both methods can also be complicated by the simultaneous presence of an element at the surface and in a covered layer.

So, great care must be taken in the interpretation of the data obtained by the depth discrimination methods. While a fully automatic separation of surface and sub-surface layers was not found feasible, the line ratio or absorption exponent maps provide complimentary information to the elemental distribution images acquired.
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4 Application Examples

As discussed in Chapter 1, a variety of questions can be investigated in historical paintings. The study of sub-surface layers is of great interest, either to identify entire paintings that were discarded and overpainted (see section 4.1) or to study *pentimenti* (see section 4.2). Both studies can provide crucial arguments in discussions concerning the attribution of a painting to an artist (see section 4.3).

The presence of hidden paint layers can in general be detected via the established methods XRR and IRR, but often insufficient information is obtained to fully explain the features visible in the resulting images. The elemental distribution images obtained by MA-XRF can provide additional information and allow to answer open questions.

It can also be crucial to know which pigments were employed in the creation of a painting and how they are distributed. This allows discriminating between original and later added paint to support conservation treatments (see section 4.4). This is often possible by means of tracers, i.e. elements only present in anachronistic pigments that were not available to the original artist. Also the pigments use of an artist can provide insight in his *modus operandi* (see section 4.5).

Often these questions can be sufficiently answered by the investigation of several spots on the surface of a painting by means of portable XRF. The number of spots to be investigated is in general limited so that the distribution of a pigment can only be determined roughly and pigments used in a small area might be missed. Furthermore, the beam size of the instrument employed also may have an influence on the results. Results obtained with a small beam may not be representative, while large beams can render it impossible to investigate small features without contributions from neighbouring paint layers.

Even if a pigment is clearly identified, the capabilities of pXRF investigations to identify the manner the paint was applied in are limited. Was the pigment used to execute the entire paint layer, or just to set a highlight? Was it used on the surface in a recent conservation treatment, or is it present in a now covered composition?

And last but not least, art-history is a visual field and elemental distribution images are in general more convincing arguments for the presence and nature of hidden features than tables of measured intensities or concentration values.
4.1 Identification of overpainted works

4.1.1 Vincent van Gogh – *Birds’ nests*

![Image of Vincent van Gogh's Birds' nests with X-ray radiograph]

**Figure 59** Vincent van Gogh, *Birds’ nests* (Kröller-Müller Museum, Otterlo the Netherlands, Late September – early October 1885, Oil on Canvas, 33.5 x 50.5 cm, KM 109.945, F108/JH940) as photograph and X-ray radiograph. Black lines in the radiograph indicate contours correlated with the surface image, red lines indicate contours correlated with the hidden painting.

While Vincent van Gogh (1853-1890) is today considered to be one of the most influential artists of the late 19th century, economic problems during his life forced him frequently to re-use canvasses and to paint over older works. It is estimated from XRR investigations that at least during his time in Paris, one third of his paintings were painted on used canvas [1]. Many of the overpainted works are known from Van Gogh’s letters are today considered “lost”, although they are present in museums, hidden
under later works. The identification of overpainted Van Gogh paintings allows to fill the known gaps in Van Gogh’s oeuvre.

*Birds’ nests* (see Figure 59) was painted by Van Gogh in fall 1885 on an already used canvas. The XRR reveals the presence of paint layers not correlated to the surface painting, but no details allowing to identify the theme of the covered painting can be discerned.

In order to obtain additional information on the covered composition, the painting was brought to DESY and investigated with the MA-XRF scanner at beamline L. Selected elemental distribution images acquired in this experiment are shown in Figure 60. The surface painting is dominated by brownish colours, which are mainly executed with earth pigments (Fe and Mn oxides). These browns were shaded by the addition of green Cr oxide pigments. Ba could also be found in the painting and is assumed to be used as an extender of other pigments in the form of sulfates. The correlation of Ba and Sr indicates that the barium sulfate used here, is from a natural origin, i.e. barite (BaSO₄) [2].

While Sb was only found in forms associated with the hidden painting, Cd was found in the surface layer, probably in the form of cadmium yellow (CdS). Its isolated occurrence in non-central areas of the painting suggests that it was used during a restoration treatment.

Ca is assumed to be present in huge abundance in the form of chalk (CaCO₃) in the ground layer. However, given the thick covering paint layers the ground is not expected to contribute to the detected Ca fluorescence radiation. The Ca signals recorded are mainly correlated to dark areas so that it is assumed that Ca is present in a dark pigment such as bone black (a black carbon based pigment that contains CaPO₄ as a remnant of the animal bones burned during its production).

The yellowish inner part of the middle nest and the yellow straws were mainly executed with zinc white (ZnO). As no element associated with yellow pigments (e.g. chromates (M(II)CrO₄) or cadmium yellow (CdS)) was found, it is assumed that these parts were executed with a mixture of zinc white and yellow lake.

Due to the absorption in the covering paint layers not all pigments used in the hidden composition could be identified. The use of pigments composed of light elements, such as Cr-based ones and earth pigments, can only be assumed.
In contrast, the use of zinc white (ZnO) and lead white ((PbCO$_3$)$_2$·Pb(OH)$_2$) as white pigments could be observed, as well as the use of the red pigment vermilion (HgS). In the hidden painting, considerable amounts of Naples yellow (Pb$_2$Sb$_2$O$_7$) were used. Ba and Sr are also present in the form of extenders, as is the case in the surface painting.

A close inspection of the Sb distribution image reveals the lower part of a painting depicting a farmer with his oxcart and a draft animal, similar to another oxcart painted by Van Gogh (see lower part of Figure 60). The orientation of the vermilion paint strokes is similar to that in *Wood Gatherers in the Snow*. So it can be assumed that the underlying composition showed a farmer, returning with his oxcart from work at sunset.

But how does this fit in Van Gogh’s oeuvre? Between mid-August and early September 1884 Vincent van Gogh wrote to his friend Anthon Gerard Alexander, ridder van Rappard:

"I’ve already got painted sketches in the finished size of something like 1 1/2 metres by 60 cm of Ploughman and Sower and Shepherd. Smaller ones of Wheat harvest and Ox-cart in winter. So you can imagine that I’m not exactly sitting on my hands these days." [Van Gogh’s letter No. 454, [3]]

The mentioned painted sketch of the Shepherd has been identified as *Shepherd with flock of Sheep* (F 42/JH 517, Soumaya Museum, Mexico City, Mexico), while the sketch of the Ploughman was found under the *Cottage with tumbledown barn and a stooping woman* (F 1669 / JH 825, private collection). The fate of the other sketches is unknown [Notes to Van Gogh’s letter No. 454, [3]].

One might consider that the smaller sketch of the oxcart was cut to pieces by van Gogh and re-used for the later painting of the *Birds’ Nests*. As no information on the size of the “smaller” studies is available, speculation of the further fate of the missing pieces of the ox-cart are not promising, as it is very well possible that these leftovers were discarded by van Gogh himself. Until now, no neighbouring pieces could be identified by weave pattern matching [4].

The results discussed in this section have been previously presented in [5].
Figure 60 Elemental distribution images of the Birds’ nests. The two images most informative on the hidden painting are enlarged and their features compared to two other paintings by Vincent van Gogh: *Wood gatherers in the snow* (Private collection, September 1885, Oil on Canvas on Panel, 67 x 126 cm, F43/JH516) and *Oxcart* (Kröller-Müller Museum, July 1884, Oil on canvas on panel, 56.7 x 82.5 cm, F38/JH504). The
elemental distribution images were acquired with a primary beam of 38.5 keV with a step size of 1 mm and a dwell time of 0.275 s per pixel at beamline L of DESY.

4.1.2 Francisco Goya – Portrait of Ramón Satué

Figure 61 Portrait of Ramón Satué, by Francisco Goya, 1823, Oil on canvas, 107 x 83.5 cm, Rijksmuseum Amsterdam as photograph and XRR.

It is long known that Francisco Goya (1746-1828) re-used canvas and overpainted older works, not only his own but also those of others. The Portrait of Ramón Satué (see Figure 61) is such a case. The presence of an overpainted second portrait was discovered in 2009 during a routine XRR investigation, but only few details could be observed (see Figure 61). The sitter of the original portrait was shown seated, wearing a high collar, sash and epaulettes, with his legs to the left and both hands visible. The formal nature of the hidden portrait is of great contrast to the casual image of Ramón Satué. However, there is no doubt that both portraits are from Goya’s hand. The portrait of Ramón Satué was executed directly on top of the original portrait and even incorporated the original sitter’s ear into the final portrait, a practise never observed when Goya overpainted works of others. Also, both paintings were executed with Goya’s typical lively brushstrokes. In order to reveal more information on the first portrait, the central part of the painting was investigated by means of Instrument B.
Of special importance were the elemental distribution images of Hg, Sb, Pb and Fe (see Figure 62). Hg is only present in a single pigment, vermilion (HgS). Sb is assumed to be present in Naples yellow (Pb₂Sb₂O₇) and the Fe distribution is the result of the use of earth pigments (Fe and Mn oxides and hydroxides). Pb is mainly present in lead white ((PbCO₃)₂·Pb(OH)₂). While the impression of the Hg containing areas to the viewer is obvious, the areas containing Sb and Fe are more ambiguous. Earth pigments can have colours from dark brown to red and yellow; while Naples yellow on its own is obviously yellow, it can be used in mixtures with other pigments to create other shades. However, it can be assumed that the golden accents of the chair and on the epaulettes were really yellow. Based on these elemental distribution images, the XRR and the colour of the original paint layer, observed at a few spots with a stereomicroscope through cracks in the surface, a reconstruction of the original portrait was made (see Figure 62).

While it is not possible to identify the sitter of the original portrait, his identity can be narrowed down to a small group of people. First of all, it can be excluded that the hidden portrait also depicts Ramón Satué, as he was a judge and not a soldier.

In the Hg distribution image, next to the red sash and the skin tones, also a red star can be recognized on the sitter’s left pectoral area. Comparison with other portraits of Spanish generals by Goya allows identifying the star as part of the insignia of the Order Real de España, a salaried chivalric order modelled after the Légion d’Honneur. In combination with the red sash, the decorations can be identified as the caballeros grandes bandas, the highest level of the order. The order was funded by Joseph Bonaparte (1768-1844), when he became King of Spain (1808-1813) and was the principal decoration worn at his court. The highest level of the order was awarded 40 times, also to Joseph himself. The plastrons visible in the Fe image allows to identify a military field uniform, probably that of the light cavalry of Joseph’s Royal Guard. It has not been possible to identify which of the fifteen high ranking officers wearing the grand banda shared the privilege of being entitled to wear such a uniform. However, written records suggest that Joseph himself was never portrayed by Goya.

Unfortunately, the other military decorations of the sitter cannot be identified. These decorations are the red ribbon under the sitter’s chin and the second red star to the left of plaque of the Orden Real. Below it,
also a second plaque can be discerned, painted with large amounts of lead white and therefore probably white or silver coloured.

Not only is the identity of the sitter mysterious, also the history of the canvas is unclear. It can be assumed that the first portrait was not created later than 1813, the end of Joseph’s reign. However, the Portrait of Ramón Satué was signed and dated in 1823, which suggests that Goya kept the portrait of a highly decorated officer of Joseph Bonaparte’s Army for ten years before re-using it. He did this, even though in the political turbulent first decades of the 19th century in Spain, the possession of such a portrait might have had dire consequences.

Another unsolved question revolves around the presence of Zn in the painting (see Figure 62). The chemical compound Zn is present in could not be identified as taking samples from the paint was prohibited, but the use of zinc white (ZnO) could be excluded as the paint did not exhibit the characteristic fluorescence of zinc white under UV irradiation. Nevertheless, the unidentified Zn compound seems to have been added deliberately to the black paint employed to execute the clothes of Don Ramón.

This section was adapted from [6].
Figure 62 Elemental distribution images of Fe, Zn, Sb, Hg and Pb and the reconstruction of the original portrait based on these results. The better part of the painting’s surface was scanned with Instrument B, with the X-ray tube operated at 35 kV and 0.2 mA, so that Sb was not properly excited. The central part of the painting was later revisited and scanned
with tube settings of 45 kV and 0.2 mA. In all scans a step size of 1 mm was employed with dwell times between 1.6 s and 2.8 s per pixel.

4.2 Pentimenti

4.2.1 Philipp Otto Runge - *Pauline im weißen Kleid*

![Figure 63](image)

Figure 63 *Pauline im weißen Kleid vor sommerlicher Baumlandschaft*, controversially attributed to Philipp Otto Runge, 1804(?), oil on canvas, 105.7x85.2 cm, private collection, Germany. Photograph (left) and XRR (right).

Figure 63 shows the painting *Pauline im weißen Kleid vor sommerlicher Baumlandschaft* (Pauline in a white dress in a summery forest landscape). The creator of the painting is unknown, but in 1988 C. Jagt attributed it to Philipp Otto Runge (1777-1810) [7]. She identified the painting as one of three portraits Runge painted of his wife Pauline and dates it to late spring 1804. The portrait shows the eighteen year old Pauline briefly after her marriage to Runge. Jagt’s arguments are beyond stylistic considerations, the similarity of the sitter to other portraits of Pauline and references to the painting Jagt identified in Runge’s letters and that the sitter’s dress is typical for the fashion in Northern-Germany between 1801 and 1806. She also points out that such a dress would typically feature a V-neck.

In earlier studies, the pigments used in the painting’s creation were identified as typical for the early 19th century. The XRR revealed
pentimenti around head and shoulders of the portrait. However, the XRR is difficult to read, due to the absorption in the ground layer(s). In order to allow for a more detailed study of the pentimenti, the painting was brought to beamline L of DESY and investigated there.

Of most interest are the elemental distribution images of Fe, present in the brownish, reddish earth pigments, Co, present in Co blue (CoAl$_2$O$_4$), Sb, present in Naples yellow Pb$_2$Sb$_2$O$_7$, Hg, present in the red pigment vermillion (HgS) and Pb, mainly present in lead white ((PbCO$_3$)$_2$·Pb(OH)$_2$) (see Figure 64). Surprisingly, Sb was not only found in the yellow areas, but also in the Hg and Pb rich skin tones. The Sb in the skin tones is assumed to result from the presence of Naples yellow as a minor component to brighten the skin tone.

The first observation is that in the face, the Pb, Sb and Hg elemental distribution images show no difference with the visible image. This indicates that the face has not been modified to change the identity of the sitter. The same elemental distribution images indicate (together with the XRR) that the original dress featured a V-neck, which originally exposed more of the sitter’s skin, as expected by C. Jagt. In a close study of the face, in the Sb distribution image one cannot avoid the impression that the sitter was not looking modestly to the left, as is the case in the final portrait, but directly at the observer.

Obvious is the presence of ribbons in the hair of the original composition, so called taenia (Latin for tape). The composition of the ribbons matches that of the belt of the final portrait. Further, the fact that the highest intensities of Co and Hg occur on the different positions indicate that the ribbons were of changeant fabric.

The collar and taenia remind scholars of Philipp Otto Runge’s drawing of his sister, who was portrayed in a similar manner (Figure 64). Hg and Sb show that the original hairstyle of the sitter was open hair, held by the ribbons hanging over her shoulders.

The presence of Hg and Sb in the original hairstyle, but not in the now visible, suggests that the hair was originally of brighter colour. This seems to contradict the assumption that the same woman was portrayed. However, literature research revealed that it was fashionable at the beginning of the 19th century for a woman to wear wigs, whose colour was adjusted to the time of the day: A black wig in the morning, a brown one in the afternoon and a blonde in the evening. So the original and
changed portrait show probably the same woman at different times of the day [8].

We believe that the portrait showed the sitter originally in a more revealing dress, with loose hair, looking straight at the observer. For unknown reasons the portrait was modified to its current, more modest appearance.

The similarity between the original portrait and the drawing of Runge’s sister is striking, and connects the Pauline im weißen Kleid to the early 19th century, when this hairstyle was fashionable. However, these findings were not considered to be convincing arguments by a number of Runge scholars and the attribution of the painting is still unchanged.

This section was adapted from [9].

Figure 64 Left: Elemental distribution images of Fe, Co, Sb, Hg and Pb. Right: Philipp Otto Runge, Bildnis der Schwester Maria Elisabeth (Portrait of (his) sister Maria Elisabeth), black and white chalk on yellow paper, 53.3x42.9 cm, formerly Pommersches Landesmuseum, Stettin, but considered lost in WW2. The painting was investigated with a primary
beam of 32 keV, a step size of 1 mm and dwell times between 0.7 s and 1.0 s per pixel.
4.2.2 Caravaggio – Rest on the Flight into Egypt

Michelangelo Merisi da Caravaggio (1571-1610) can be considered one of the most famous and influential painters of Western Art. Despite his fame, contemporary written records of his life are fragmentary, as he was forgotten soon after his death. Already during his life his studio practise attracted considerable interest, but reliable sources for it are scarce. Thus, scientific methods are needed to gain insight into his *modus operandi*. *Rest on the Flight into Egypt* (Figure 65) is one of the earliest large canvases by Caravaggio, painted between 1596 and 1598.

In this painting Mary, Jesus and Joseph are resting on their flight into Egypt and are accompanied by two music playing angels and their beasts of burden. The painting’s background features a landscape with open sky, which is somewhat unusual for the artist, who is best known for placing his models before a dark, often non-descriptive background.

The painting was investigated in the framework of a larger investigation of Caravaggio’s pigment use and painting style, focussing on the two versions of *St. Francis in Meditation* discussed in section 4.5.1. While elsewhere in the painting no major *pentimenti* were found, the position of Mary has been adjusted at least once, as it is shown in Figure 65.

The final impression of the painting is well discernible in the Fe distribution image, showing the distribution of the reddish/brownish earth pigments. Hg is present in the red pigment vermillion (HgS) that was used to model the flesh tones and red clothing of Mary. Cu is mainly present in the landscape in the background and in the dark skirt of Mary. It is correlated to a green pigment. Sn is assumed to be present in the form of lead tin yellow (type I: Pb₂SnO₄ or type II: PbSn₁₋ₓSiₓO₄), which was at times added to the green Cu pigments to counterbalance their bluish tone and render the paint more opaque.

In the enlarged Hg-L image, it is obvious that Mary’s ear was originally positioned further to the left. The original version of the ear, indicated by the red arrows, was overpainted when her head was shifted to the right.

When the leaves visible in the Cu and Sn-K elemental distribution images are compared with those visible in the painting, it is apparent that only the leaves in the Cu image are in good agreement with it. Many leaves visible in the Sn image are not visible on the surface of the painting. It can be concluded from this findings that the leaves originally painted at the right edge of the painting were overpainted, possibly when the position of Mary was adjusted.
The current position of Mary’s red sleeve is indicated by the yellow line. If this line is transferred to the Sn elemental distribution image, it becomes clear that several of the Sn containing leaves extended under Mary’s sleeve. Apparently the abundance of Sn in the overpainted leaves was higher than in currently visible ones, which might suggest that they were originally painted in a brighter tone.

The *pentimenti* that were revealed by this investigation confirm the status of the painting, which is generally accepted to be a first version by the hand of Caravaggio himself. These findings give additional insight in the studio practise of Caravaggio, as they clearly illustrate how he adjusted the composition of his (early) paintings during the creation process.

The painting was investigated in the framework of the experiments for [10].
Figure 65 Rest on the Flight into Egypt, 1596-1598, oil on canvas, 135.5 x 165.5 cm, Rome, Galleria Doria Pamphilj, photograph and elemental distribution images of Fe, Cu, Sn and Hg. The yellow line indicated the final position of Mary’s arm and the red arrows the original position of
her ear. The area was investigated by means of Instrument D with a step size of 1 mm and a dwell time of 0.25 s per pixel.
4.3 Attribution of paintings

4.3.1 Rembrandt van Rijn – Portrait of an Old Man
As discussed in chapter 1, in the framework of 17th century Old Master Paintings the term “underpainting” generally refers to the first painted sketch of a composition. It is applied to a prepared ground often using a monochrome, brownish oil paint to roughly indicate light, shade and contours. So far, methods to visualize this type of underpainting - other than in localized cross-sections - have been limited. Neither IRR nor NAAR have proven to be practical, adequate visualization tools. As the study of the underpainting allows an insight in a painting’s genesis, it can provide valuable information about the attribution of a painting.

Such was the case for Portrait of an Old Man, which at the moment of the MA-XRF experiments, was attributed to the workshop of Rembrandt and considered to be part of a larger group of paintings showing an identical bearded old man. All these paintings were considered copies after an original that was thought to be lost. However, during the conservation treatment of the present painting, the authoritative Rembrandt Research Project started to reconsider the painting’s former classification as a studio work, based on art historical, stylistic and technical arguments. It is worth noting that the support of the painting was originally of rectangular shape, which was later changed to the oval shape shown in Figure 59. During the restoration treatment prior to the MA-XRF experiments additional pieces of wood were added to the painting’s support to restore the rectangular shape.

During the conservation treatment of the painting in Amsterdam covered paint layers, hidden below the surface, became apparent. To study their distribution, IRR and XRR investigations were done (see Figure 66). Both IRR and XRR revealed isolated compositional changes or pentimenti, mostly to the man’s headgear, the position of his shoulder as well as alterations in the figure’s collar. It was expected that a visualization of the underpainting could reveal the first compositional sketch and therefore provide insight into the object’s genesis and, hence, its attribution. However, neither XRR nor IRR gave easily/straightforwardly interpretable information that provided insight into the paint build-up, let alone its original appearance.

In an attempt to visualize the underpainting, the Portrait of an Old Man was brought to the NSLS where it was investigated by the MA-XRF scanner at beamline X7A. The findings in these scans were confirmed by.
a paint cross-section prepared from a sample taken from the painting, investigated by SEM-EDX.

In Figure 68 elemental distribution images of four elements (Fe, Cu, Hg and Pb) are shown that provide an insight in the hidden paint layers and those at the surface. Fe is present in earth pigments that were used to paint the surface composition, especially the old man’s clothes and the shadows in his face. Other earth pigments were used in an overpainted sketch of features in the background, possibly including a horizon in the lower right corner. Also, the hat that is visible in the IRR is faintly discernible in this image. Otherwise the Fe distribution image is not very informative regarding the hidden paint layers, mainly due to the high abundance of earth pigments in the surface painting. The Hg distribution image indicates the area where vermilion (HgS) was used to set the highlights in the flesh tones of the old man’s face. The original headgear of the person sketched is visible as a faint shadow, as in the IRR image, suggesting that Hg might be present throughout the painting in low abundance. The Pb distribution image offers information comparable to the XRR, albeit with a considerably reduced contribution from the wooden panel. The Cu distribution image is not correlated to the surface painting, but visualizes the underpainting applied to sketch a self portrait in the style of Rembrandt (Figure 68) by filling in the background and leaving a ‘reserve’ for the figure in the foreground. Based on the Pb and Cu distribution images, the main contour lines of the original portrait could be reconstructed, which shows a strong resemblance to other self portraits of Rembrandt, such as the one present at the National Museum of Sweden in Stockholm. The absence of the hidden portrait in the Fe and Hg distribution images lead Rembrandt scholars to the conclusion that the original representation was left unfinished and overpainted with the portrait of the old man that is now visible.

The pigments in the underpainting were unknown. Cu is present in blue and green pigments used in the 17th century, but a clear green or blue background was not expected considering similar paintings by Rembrandt. To identify the pigments, a paint sample was taken.

The sample, representing all layers of the painting down to the ground, was taken from the upper right corner of the painting, as indicated in Figure 68. During the preparation of the sample, the surface paint layer and the varnish layer detached themselves from the rest of the sample and were lost, but the layers containing the underpainting and the ground were preserved. In Figure 67, three layers can be discerned in the
elemental distribution images acquired by SEM-EDX. From the bottom, it is possible to distinguish between the chalk (CaCO₃)-containing ground layer, followed by a Pb rich imprimatura layer on which the underpainting layer was applied. EDX spectra were acquired at several spots in order to confirm the presence of the elements indicated in the figure. These measurements also revealed the presence of Co in the Si-rich glassy smalt particles. The underpainting contains a wide range of pigments including copper green (probably verdigris, a Cu corrosion product), earth pigments, smalt (ground Co-rich glass), lead white ((PbCO₃)₂·Pb(OH)₂), carbon black and potentially calcite (mineral CaCO₃), resulting in a brownish/greenish colour.

It is assumed that palette scrapings were used to execute the underpainting. There is no apparent reason why an artist should have mixed these pigments deliberately to create a brownish tone that would have been difficult to be reproduced, and did not choose a simpler mixture of pigments. Each evening the palettes in a workshop were cleaned by scraping off the dried paint. These (in sum brownish) scrapings could be recycled by mixing them in oil for sketching.

This case illustrated that it is possible to visualize the underpainting below the surface of a painting by means of MA-XRF, which was not possible by using the conventional imaging techniques IRR and XRR.

The reconstructed sketch of an unfinished self portrait, in combination with a detailed study of the painting technique used to execute the painting and indirect literature references, provided proof for the painting’s authenticity, as it is highly unlikely that a copyist would have started and aborted a copy of a self portrait in order to copy another painting by Rembrandt. These material indications were considered so convincing that the painting was acknowledged by the Rembrandt Research Project and exhibited from December 2011 to October 2012 in the Rembrandthuis Museum, Amsterdam, as an original painting by Rembrandt van Rijn. Furthermore, it was demonstrated that the underpainting in this panel consists of a highly heterogeneous mixture of pigments, including copper-containing ones, probably palette scraping.

This section was adapted from [11] with kind permission from Springer Science and Business Media.
Figure 67 Microscopic image and secondary electron image (SEI) of the paint sample’s cross section with elemental distribution images acquired.

Figure 68 Elemental distribution images of Fe, Cu, Hg and Pb. Lower left: silhouette of an unfinished self portrait of Rembrandt, superimposed on the Cu distribution image. Lower right: Rembrandt van Rijn, Self portrait, 1630, 15.5×12 cm, National Museum of Sweden (Stockholm). The red ‘+’ indicates the location from where a paint sample was taken. The
elemental distribution images were acquired with a step size of 0.1 mm and a dwell time of 8 ms at the NSLS. The Hg-L distribution image was corrected for the interference of Hg-L and Pb-L fluorescence radiation as described in section 2.2.2.2. Adapted from [11] with kind permission from Springer Science and Business Media.

4.3.2 Vincent van Gogh – Flower Still Life
The investigation of Vincent van Gogh’s Flower Still Life with Meadow Flowers and Roses has catalyzed considerable technical progress in this project and its re-attribution to Van Gogh can be considered one of the most important results of this project in the art-historical field. In this section the reasoning behind the re-attribution of the painting to Vincent van Gogh is presented.

The canvas first surfaced at the beginning of the 20th century as one of several works of Vincent van Gogh in the collection of Lodewijk Cornelis Enthoven (1859–1920). While this work was criticized early on as being unbalanced and of inferior quality compared to other works by Van Gogh, it was not until 2003 that the painting was dismissed and attributed to an unknown artist [12].

At the time of the dismissal, it was already known from X-ray radiography (XRR) that under the surface of this painting, a scene depicting two wrestlers was present. This scene is of specific interest, since during his brief stay at the Antwerp Academy of Fine Arts (Belgium), where he studied painting under the guidance of Charles (Karel) Verlat, Van Gogh wrote to his brother Theo: “This week I painted a large thing with two nude torsos—two wrestlers, a pose set by Verlat. And I really like doing that.” (Van Gogh letter Nr. 555, [3]). The painting described in the letter was considered lost at the moment of our research. The XRR image of the Flower Still Life reveals too few details of the wrestlers to compare them with other works of Van Gogh; one of the reasons for this is that the strongly X-ray absorbing flowers in the visual upper painting obscure the view.

To gain additional insight in the painting’s composition, several sub-areas of the painting were scanned by means of the DESY scanner and the mobile Instruments C and D. This allowed for a direct comparison between these scanners (see chapter 2). As it was not possible to observe the hidden composition by scanning through the surface, the painting was scanned from the backside (see chapter 1), which necessitated a correction for absorption artefacts (see chapter 3). The elemental distribution maps best suited for the study of the overpainted wrestling scene are shown in Figure 69.
Several distinct arguments can be brought forward to strengthen the attribution of the painting to Van Gogh himself.

*Experimental pigment use in the upper painting and imbalance of the composition.* When he arrived in 1886 in Paris, Van Gogh was influenced by the colours of the Impressionist paintings he discovered, prompting him to start experimenting with colours and pigments himself. These experiments mostly resulted in flower still lives, as these did not require costly models. The experimental nature of the flower still life is well illustrated by the parallel use of multiple pigments of the same colour (see section 4.5.2). A close optical inspection of the flower painting and the way the paint was applied by the artist reveal that the painting was executed in at least three separate steps. First the upper part was painted, probably from a real life model where the mass of flowers in the vase is covering the body of the right wrestler. In a second step the flowers of the lower part (covering the left wrestler) were painted and in a final step various decorations were added. The knowledge of the presence of the wrestling scene below the surface helps to understand better the lack of balance that can be observed in the flower painting: in order to prevent the light tones of the skin of the wrestlers to shine through, it was necessary to use contrast-rich paint and many details in these areas.

*The canvas with the wrestling scene and Van Gogh’s stay in Antwerp.* Both the dimensions of the canvas as well as a number of details in the wrestling scene suggest that it was first painted during Van Gogh’s brief stay at the Antwerp Academy of Fine Arts. Although he at first was not admitted to the painting classes (only to the drawing classes), he could convince his teachers to also let him study painting. As explained in one of his letters ["Now I ought to have had a large canvas by Monday — I’ve also been explicitly told that I have to have other brushes &c. besides what I have.” Van Gogh letter Nr. 554, [3]], upon their insistence, he bought new painting materials, including a new canvas to paint on. While the canvas he obtained was extraordinary large for him, for the Academy of Fine Arts in Antwerp it was a standard format and often used there, as witnessed by the award-winning paintings of the “Prix de Rome” contest. In another letter [Van Gogh letter Nr. 555, cited above], he describes that during a painting class lead by the Academy director Verlat, he painted on this canvas two wrestling men with loincloths (see right part of Figure 69). The later is of importance given the fact that in most art academies of that time, male models posed naked, while in Antwerp the loincloth remained in use until ca. 1890. Also the brush width with which
the painting was executed is similar to that of his other Antwerp paintings, as is the palette used. Other specific details of the wrestling scene uncovered by MA-XRF also are consistent with Van Gogh’s way of painting in Antwerp: Next to the Zn distribution image, that gives us the best view on the two figures as a whole, the Ba and Hg elemental maps of the hand of the right figure grappling the arm of the left wrestler are of interest. As shown in Figure 69c, the hand is painted with a limited number of rough strokes very similar to the manner in which the hands in Vincent van Gogh’s *Potato eaters* were painted. Van Gogh painted this work one year before his stay in Antwerp. The brush strokes are visible in the Ba map presumably because of the fact that barium sulfate (BaSO\(_4\)) was used as extender of the paint being used.

We also see that vermilion red (Hg distribution) is used to paint reddish haloes around the fingers and arm. This manner of outlining is very similar and possibly an imitation of the custom of the Antwerp painters Rubens and Jordaens that impressed Van Gogh [“I’m utterly carried away, for instance, by [Rubens’] way of drawing the features in a face with strokes of pure red or, in the hands, modelling the fingers with similar strokes. I go to the museum quite often and then look at little else but a few heads and hands by him and Jordaens” Van Gogh letter 547 [3]].

*Van Gogh’s habit of overpainting during his Parisian period.* From the 87 paintings from the Paris period in the collection of the Van Gogh Museum, 25 have been painted over older works and only from January 1887 Van Gogh started scrapping off the old works before painting on the original canvases. Together with the fact that the flowers depicted on the painting were available only in spring and summer we conclude that the painting was executed in early summer 1886.

*The significance of cracks in the surface painting.* An important number of cracks are present in the surface painting. Again the knowledge about the presence of the wrestling scene below the surface is useful to explain this. While in the surface painting the main white pigment is lead white ((PbCO\(_3\))\(_2\)·Pb(OH)\(_2\)), a fast drying pigment, in the covered wrestlers, zinc white (ZnO), a considerably slower drying paint, was used. As the paint of the wrestlers had not completely dried, at the moment the flower still life was painted over it, cracks formed in the surface painting during the drying of both paintings. While it cannot be excluded that another artist painted a flower still life in the style of Van Gogh, be it for fraud or to train his own skills, the chances that this was done on a still wet painting
of two wrestlers painted in the style of the Antwerp Academy of Fine Arts are quite small.

**Signature.** In the upper right corner a signature “Vincent” can be discerned. The authenticity of it has been often doubted, claiming that this area of the painting had been polished before applying the signature or that it is on an intermediate layer of varnish. Neither is true. The signature is located directly on the painting. The varnish on the signature had not been removed, so that it is indeed covered by at least two layers of varnish that give it a slightly strange shine.

On the basis of the above five considerations, we believe to have convincingly reconstructed the material past of ‘Flower still life’ and have strengthened its attribution to Vincent van Gogh.

This section was adapted from [13] with kind permission from Springer Science and Business Media.
Figure 69 *Flower Still Life with Meadow Flowers and Roses*, previous attribution: unknown artist, beginning of the 20th century; current attribution: Vincent van Gogh, summer 1886 (Kröller-Müller Museum, Otterlo, the Netherlands. Oil on canvas, 100×80 cm, KM 100.067, FH 278, JH 1103). a) photograph (rotated by 90 degrees) and b) XRR. c) is a magnified detail of the elemental distribution images of Zn, Ba and Hg shown in the right part of the figure superimposed on the XRR. The yellow dashed lines indicate the area of the hand shown in detail. The contour of the two wrestling figures was sketched in to guide the eye. The red dashed lines indicate the area investigated with the Instruments B and C to identify the pigments used in the flower still life (see section
4.3.2). This figure was adapted from [13] with kind permission from Springer Science and Business Media.

4.4 Identification of later added paint layers

4.4.1 Rembrandt van Rijn and/or studio - Saul and David

Figure 70 Rembrandt and/or Studio, Saul and David, c.1655, Mauritshuis inv. no. 621 / Bredius no. 526, oil on linen, 130.5 x 164.5 cm. In the XRR (right) the joins between the different pieces of canvas are clearly visible. The red dashed lines indicate the area investigated by MA-XRF, the yellow dashed ones the area of the painting shown in the XRR. The joint is indicated in the XRR by red arrows.

Saul and David, shown in Figure 70, is attributed to the workshop of Rembrandt van Rijn with a disputed attribution to the master himself.

At the moment of the investigation, the painting was covered by a thick layer of darkened varnish and possible overpaint. It was being studied prior to eventual conservation treatment. The planning for this was not straightforward, as the extent of original paint still present in the painting was unknown, due to its complex history. Moreover, the authenticity of the curtain depicted in the area between the figures was questioned.

At an unknown moment in the past the painting was cut into two separate paintings. The reason for this is unknown. Based on dimensions listed in the auction records the two figures were rejoined between 1830 and 1869. The join between the two pieces of canvas is clearly discernible in the XRR. Examination with the stereomicroscope revealed, that much
of the curtain visible in the background of the painting was added after the parts were rejoined to visually blend them together. Further, it was known from light microscope and SEM-EDX studies of paint cross sections that the original smalt-rich paint is still present under the surface of the curtain, but its exact extent was unknown.

In the art historical literature it was also speculated that originally other figure(s) were shown in the painting and that these had been removed during the cutting/rejoining of the canvas and its remnants covered by the curtain.

These questions could not be answered by conventional techniques such as XRR and IRR as the lead white \( ((\text{PbCO}_3)_2 \cdot \text{Pb(OH)}_2) \) rich ground that also contains black pigments and the dark, bone black and earth pigment (Fe and Mn oxides) rich figures yield only low contrast images with these methods.

To establish the authenticity of the curtain and possibly confirm the presence of other figure(s) the distribution of pigments in the painting was studied with Instrument C in the conservation studio of the Mauritshuis Museum.

![Figure 71](image)

**Figure 71** Elemental distribution images of Fe, Co, Ni and Cd acquired with Instrument C operated at 50 kV, 1 mA using a step size of 1 mm and an average dwell time of 1.2 s.

In Figure 71 selected elemental distribution images obtained from the central part of the painting are shown. The distribution of Fe visualizes the earth pigments, which in general have a brownish/reddish colour and
were used in the original as well as in the later added paint. Since the curtain was mainly executed in these pigments, its folds are clearly visible in the Fe image.

Cd is present in low abundance and it is unclear whether it is present as a drier or as a pigment, but as Cd salts were not used until the 1840s they are good tracers for later restoration treatments and indicate heavy reworking of the area along the join.

From paint cross sections investigated by SEM-EDX it is known that Co is present in two compounds: smalt (ground Co rich glass used as pigment in the 17th century) and Co salts added as drier to paint in the 19th century. These two compounds cannot be differentiated by the Co signal alone. However, since Co ores also contain Ni the compounds synthesized from these minerals feature a characteristic Co/Ni ratio. In the Co/Ni scatter plot in Figure 72, the Co associated with smalt and that used as a drier can be clearly distinguished; the distribution of these two Co containing compounds can be visualized by colouring the Co distribution image in Figure 72 accordingly.

The smalt distribution image reveals the folds of the original curtain and shows that under the surface a considerable amount of the original paint is still present, except in the area directly along the join, where much of the original paint was removed. Furthermore, this disproves speculations about possible other figures in the painting as also in the original composition a curtain filled the centre of the painting.

This case illustrates the value elemental distribution images can have for the planning of a conservation treatment if conventional imaging techniques fail to obtain the required information. The visualization of the distribution and the extent of the original and the later added paint by the use of two tracers, Cd and the Co/Ni ratio, made it possible for the conservator to make a more accurate description of the painting’s true condition and an informed conservation treatment proposal taking this new information into account.

These results, obtained in collaboration with Petria Noble of the Mauritshuis Museum, have been have been published in [14].
Figure 72 Co map colourized based on the Co/Ni ratio to visualize the extent of original paint.
4.4.2 Master of the Portraits of Princes - Portrait of Engelbert II

Figure 73 Master of the Portraits of Princes, Portrait of Engelbert II, Count of Nassau, Rijksmuseum Amsterdam, ca. 1480 - ca. 1490, oil on panel, 33.5 x 24 cm. Left: The painting during the investigation by MA-XRF, before removal of later additions (image (c) L. Sozzani), right: after restoration treatment (image (c) Rijksmuseum Amsterdam).

The painting shown in Figure 73 features Engelbert II, Count of Nassau (1451-1504), who is identified by the letters under the portrait ("Engelbert Conte de Nassau"). He is depicted as a falconer wearing the chain of the Order of the Golden Fleece prominently around his neck. The painting is attributed to an unidentified artist, who is called the Master of the Portraits of Princes and the work is assumed to be created in the period between 1480 and 1490.

The painting has been subject to restoration in 2010, which involved the removal of later additions. In the left part of Figure 73, the painting is shown after the removal of clearly discernible earlier repairs, the state in which it was investigated; to the right it is shown after the treatment and the removal of later additions.

Prior to the investigation by MA-XRF the painting was thoroughly investigated with a stereomicroscope, which revealed that the costume of
the sitter had been altered through numerous previous restoration interventions and it was difficult to discern the true form of the costume.

Visual inspection of the letters below the portrait reveals that the spacing of the word “Engelbert” is different from that of the words “Conte de Nassau”. A XRF measurement revealed the presence of the elements Cr and Sn. Cr is associated with yellow chromate pigments (of the type M(II)CrO₄) that were used as pigments from the 19th century onwards, while Sn is present in the yellow pigment lead tin yellow (type I: Pb₂SnO₄ or type II: PbSn₁₋ₓSiₓO₄), which was used in painting until the 18th century. This gave rise to the suspicion that originally a different name was written in lead tin yellow that was later overpainted in the 19th century.

In order to reveal whether the name was changed and to identify later additions to the painting two areas of the painting were investigated by means of Instrument B: The letters below the portrait and the portrait itself.

![Image of elemental distribution images](image_url)

**Figure 74** Detail of the letters below the portrait as photograph and elemental distribution images. These data were acquired by means of Instrument B with a step size of 0.5 mm and a dwell time of 0.3 s.

In Figure 74 the elemental distribution images of the area of the letters are shown. The Pb distribution, which with the exception of the Pb in the letters, results from a layer below the surface, indicates that at an unknown point in the past the frame was damaged and a substantial amount of paint was lost. When the Cr and Sn distribution images are compared it is obvious that Cr was not used to write a new name, but to complete the remnants of the damaged letters that were originally
executed in lead tin yellow. Next to the yellow pigment, which is assumed to be lead chromate (PbCrO₄) due to the Pb/Cr correlation, Cr seems to be also present in retouches of green areas of the frame.
Figure 75 Elemental distribution images of the *Portrait of Engelbert II of Nassau* acquired by means of Instrument B with a step size 0.5 mm and a dwell time of 1.2 s.

A comparison between the elemental distribution images of the portrait shown in Figure 75 and the photograph of the final portrait reveals additional information on the original appearance of the painting.

Vermilion (HgS) is present in the flesh tones and the chain around the sitter’s shoulders, but it was mainly used to fill the background. The reserve originally left for the sitter is well discernible and differs considerably from the visible portrait. The reserve is smaller, with thinner arms and lower shoulders. Also to the left of the sitter no reserve for his hair is left. The original shape of the hat, which is more a cap, open to one side, is well discernible in this distribution image.

Pb is mainly present in lead white \( ((\text{PbCO}_3)_2\cdot\text{Pb(OH)}_2) \), but also in lead tin yellow (type I: \( \text{Pb}_2\text{SnO}_4 \) or type II: \( \text{PbSn}_{1-x}\text{Si}_x\text{O}_4 \)), and was used throughout the portrait. It clearly indicates the accents set, e.g. in the clothing, where the sleeves are connected to the shirt of the sitter. The Au-L distribution image confirms the gilding of the frame.

Sn is present in lead tin yellow and was mainly used in the chain of the Order of the Golden Fleece, but also in the glove and to a lesser degree to paint the falcon. The chain visible in the Sn distribution image is one link shorter than in the visible image. This additional link was necessary when the clothing was extended and painted using a Fe containing pigment.

Zn is on the one hand correlated with the Cu-containing pigment and on the other hand present in the black paint used to extend the clothing of the sitter, constituting an excellent tracer for later additions. The chemical compound Zn is present in could not be identified.

The Cu distribution image reveals together with the Ca image that what appears today as uniform black clothing was painted with two different paint mixtures. The pigment with which Cu is associated was not identified, so that no conclusions of the artist’s original intention can be drawn. Verdigris, a collective name for blue and green corrosion products of Cu, has been described as an unstable pigment, which might explain the fading of colour [15]. Cu is also present in the pins used to close the cap.
Fe is present throughout the painting and was used to model the sitter’s hair and the glove on which the falcon is sitting. It is probably present in Fe oxide earth pigments of yellow, brownish or reddish colour.

The elemental distribution images supported the conservation treatment of the portrait, as they helped identifying original and later added paint. It was so possible to remove the much later paint revealing the original costume of the sitter.

These results were obtained in collaboration with Laurent Sozzani of the conservation studio of the Rijksmuseum Amsterdam. A joint publication on the painting’s conservation history, including a detailed discussion of the treatment history of the frame, is in preparation.
4.5 Studies of pigment use

4.5.1 Caravaggio – Two versions of St. Francis in Meditation

As discussed above, the contemporary written records of Caravaggio’s life are fragmentary. They allow for a direct attribution of only few paintings, mainly those commissioned by a public institution. A great number of paintings done as private commissions have been attributed to him based primarily on stylistic and compositional considerations, and the existence of a provenance based on primary documentation such as inventories.

One of the most important historical sources on his work is Giovan Battista Bellori’s “Vite de’ Pittori, Scultori et Architetti moderni” (Rome, 1672) in which he states that Caravaggio avoided the use of cinnabar red (HgS) in his figures, as it was a “poison of tints”.

Cinnabar is the pigment derived from the mineral cinnabar, which is chemically identical to the synthetic vermilion. As these pigments cannot be distinguished by XRF analysis both will be referred to as vermilion. It is also not likely that Bellori intended to distinguish between these two pigments, as the current usage of these terms was not established at his time. While from XRF spot analysis of paintings by Caravaggio the usage of vermilion, especially in red drapery and clothing is long known, the usage of this pigment in the flesh tones is in general not accepted as compatible with his painting technique [16].

This is of great interest in case of the two versions of St. Francis in Meditation, shown in Figure 76. These two paintings belong to a group of five paintings, showing the same representation. These paintings have been attributed to Caravaggio based on stylistic considerations and indirect references in written documents. Which of the paintings is the first version and which are copies by other artists or even Caravaggio himself has been subject to controversial discussions.

Today, the Carpineto version, on display in the Galleria Nazionale d’Arte Antica in Rome (Italy), is considered to be the original painting, while the Cappuccini version, on display in the church of Santa Maria della Concezione is considered to be a copy after an original. However, it was considered the original version of the painting for many years prior to the discovery of the Carpineto version [17]. Although this attribution is generally accepted, still some doubt remains, especially as in earlier local XRF investigations in the flesh tones of the Carpineto version vermilion was found to be present.
Both versions were investigated by means of Instrument C to compare both technique and pigment use. Furthermore, several autograph paintings, i.e. paintings in which Caravaggio’s authorship is not doubted, were scanned to compare the findings.

Considerable differences in pigment use in both versions of *St. Francis* were found. When in Figure 76 the Hg distribution images are compared it is obvious that all flesh tones of the Carpineto version were executed with vermilion, including the exposed part of the shoulder, while in the Cappuccini version no Hg is found to be present (the lines visible are detection artefacts).

Instead the flesh tones in the Cappuccini version were executed with earth pigments (indicated by the high Fe intensity visible in Figure 77), possibly in a mixture with an organic red lake. A comparison of the Fe distribution images of both paintings reveals that earth pigments were used to model the background of the Carpineto version; in case of the Cappuccini version this was done by using a, probably green, Cu-containing pigment.

Cu is also found present in the Carpineto version: not in the pictorial layers, but heterogeneously distributed in the ground of the painting. If several spots on the background were investigated by XRF the fluctuating signal would be challenging to interpret, especially as ambitious researchers might interpret it as a reserve left for an unfinished painting, similar to the case discussed in section 4.3.1. (Previous researchers investigating the painting by XRF interpreted their results correctly and did not make this mistake, as discussed in [10].) The shape of St. Francis is discernible in the Cu distribution image due to absorption in covering paint layers.

In the Pb distribution image (see Figure 78) it can be discerned that the background of the Carpineto version contains considerably less Pb than the Cappuccini version. This is in good agreement with the observation that the ground layer of the Cappuccini painting is of a much lighter tone than that of the Carpineto painting and most autograph paintings of Caravaggio.

An interesting detail is the rope belt. While in the photographs it is only visible around the hips of St. Francis, the rope continues in the Pb-L distribution image of the Carpineto version in the shadowed area above the cross. It is today only barely discernible with the naked eye. The rope is not visible in the Pb-L distribution image of the Cappuccini version, but
in the Mn distribution image (not shown), which suggests an execution using the earth pigment umber (a mixture of Fe and Mn oxides and hydroxides). This difference could be explained by assuming that a copyist, duplicated with some uncertainty a detail of the painting that was difficult to see on the original.

With the exception of the Cr map, in all elemental distribution images of the Carpineto version lacunae (gaps with missing material) are observed in the area of the skull, running down to the lower left. The material used to fill the lacunae contains Cr, which is probably present in a Cr oxide green pigment and/or as a drier. The presence of Cr marks this layer as an anachronistic repair.

Given this difference in pigment use, it is highly unlikely that both paintings were created in the same workshop at the same time. But is the presence of vermilion in the flesh tones an argument against Caravaggio’s authorship of the Carpineto version?

To gain additional insight into the pigment use, three autograph paintings of Caravaggio were investigated by means of Instrument C and D in their respective galleries: Rest on the Flight into Egypt (1596-1598) and Penitent Magdalene (1597) from the Galleria Doria Pamphilji in Rome and Supper at Emmaus (1606) from the Pinacoteca di Brera in Rome.

The results obtained from Rest on the Flight into Egypt were already discussed in section 4.2.2. Excerpts of the results obtained on Penitent Magdalene are shown in Figure 79 and from Supper at Emmaus in Figure 80.

The pigment use in Magdalene’s face is similar to that in the Carpineto version of St. Francis. The flesh tones are executed with vermilion on a Cu containing ground. The strong Cu signal in the upper part of the scanned area is the result of a filled-in lacuna.

In the Rest on the Flight to Egypt also vermilion was found to be present in the flesh tones of most figures. However, as no non-descriptive background is present in this painting, a comparison of this aspect is not possible.

The pigment use in Supper at Emmaus, however, is different from the Carpineto version. No vermilion was used in the flesh tones that were probably executed in a mixture of earth pigments and/or organic lakes. The dark background contains Cu and Pb.
The results presented in this section are limited by the fact that no quantitative information was obtained that allows to compare the mixture of pigments. However, it appears that the use of vermilion is a significant feature of Caravaggio’s painting technique in at least his early Roman production. Possibly in his late works he avoided using vermilion in the flesh tones, as suggested by the results obtained from *Supper at Emmaus* (1606).

The Carpineto painting of *St. Francis in Meditation* is controversially dated between 1603 and 1606. In terms of pigment use, the presence of vermilion appears much closer to his early paintings (*Rest on the Flight to Egypt* (1596-1598) and *Penitent Magdalene* (1597)).

If the use of vermilion is allowed to be the defining criterion, our results suggest that Carpineto version was painted at an earlier date, in a period when Caravaggio still used vermilion, and moreover that the statement of Bellori referring to Caravaggio’s avoidance of cinnabar red in his figures, is not true for the early paintings. However, too few paintings were investigated to allow for comprehensive statements and a wider study of Caravaggio’s use of pigments employing MA-XRF scanning is desirable.

The full study from which these excerpts were taken is published in [10].
Figure 76 Caravaggio, St. Francis in Meditation. Left: Carpineto version (c. 1606, oil on canvas, 128.2 x 97.4 cm, Galleria Nazionale d’Arte Antica, Rome). Right: Cappuccini version (1610-1617, oil on canvas, 128.5 x 97.5 cm, Church of Santa Maria della Concezione, Rome). Photograph and Hg distribution image. Canvas size and dating according to [17]. The painting was scanned by means of Instrument C with the X-ray tube.
operated at 50 kV and 1.0 mA, a step size of 1 mm and a dwell time between 0.6 s and 2.0 s.

Figure 77 Carpineto (left) and Cappuccini (right) version of St. Francis in Meditation as Fe and Cu distribution image.
Figure 78 Carpineto (left) and Cappuccini (right) version of St. Francis in Meditation as Pb and Cr distribution image.
Figure 79 Detail of the elemental distribution images (Fe, Cu, Hg and Pb) obtained on Penitent Magdalena. The painting was investigated with Instrument D (45 kV and 0.2 mA) with a step size of 1 mm and 0.5 s dwell time per pixel.

Figure 80 Detail of the elemental distribution images (Fe, Cu, Hg and Pb) obtained on Supper at Emmaus. The red lines indicate the investigated area. The results were obtained by means of Instrument C with 50 kV, 1 mA a step size of 1 mm and a dwell time of 0.5 s per pixel.
4.5.2 Vincent van Gogh - Flower Still Life

Due to the progress of science and industry in the 19th century, new pigments became available to artists, often just being different shades of the same colour, resulting in a range of available pigments that was larger than ever before.

In simple cases an identification of the pigments used based on XRF spot measurements is possible. In complex cases, e.g. when several superimposed paint layers and mixtures of pigments are present, this is less straightforward. The Flower Still Life with Meadow Flowers and Roses is such a complex case, which has been already discussed above (section 4.3.2). Not only does the painting consist of two superimposed paintings, the flower still life was also used by Van Gogh to experiment with the pigments available to him.

So, next to using the Zn, Hg and Ba maps (see Figure 69), to visualize better the composition that was later covered, the MA-XRF maps pertaining to chemical element that are present in the more superficial paint layers can be used for other purposes. In first instance it is fairly straightforward to employ the distribution of an element in combination with the visible shapes and their colour to identify the pigments employed. On a more advanced level, it is also possible to infer from these MA-XRF maps that Van Gogh experimented with different pigments either in pure form or as mixtures and was using different pigment combinations to achieve (superficially) similarly coloured features. To illustrate this, the MA-XRF maps obtained from a multi-coloured 40x40 cm² area of the painting in which a variety of flowers in depicted are discussed in detail below (see Figure 81).

The easiest pigment to identify is the red pigment vermilion (HgS), as the element Hg is not present in any other artist pigment. However, this does not explain all red areas in the area under consideration. For example, at point ‘a’ in Figure 81, in the brown-reddish part of the flowers only Pb is abundantly present, but no other element that might be associated with red or brown colours; this leads use to deduce that this colour presumably has been painted either with minium (Pb3O4), a reddish-orange lead compound or a mixture of lead white ((PbCO3)2·Pb(OH)2) with an organic red dye. However, the latter would result in a much brighter colour than what is observed here. Apart from minium, the majority of the Pb in the painting is present in the form of lead white, while a minor amount is also present as lead chromate and Naples yellow (see below). The second white pigment used in this painting is zinc white.
(ZnO), but it was used in lesser amounts in the upper paint layers of *Flower Still Life* than in the underlying wrestling scene.

Iron oxide earth pigments were also employed, for example to paint the hearts of the bright flowers at location ‘b’ in Figure 81. While all flowers are superficially similar in colour, in the Fe image it becomes clear that only two of the flower hearts are painted using an earth colour pigment while the other one was realised using a pigment combination involving Cr, Mn and Pb. It appears very likely that chrome yellow (PbCrO$_4$) was employed. The presence of Mn might be explained by the addition of umber (Mn and Fe oxides and hydroxides) to the pigment mixture. In the petals of this flower considerably more lead white is present than the other two.

It is assumed that the Fe is also present in the form of Prussian blue (M(1)Fe(III)[Fe(II)(CN)$_6$].n H$_2$O, with M being K, Na or NH$_4$); this pigment is difficult to detect by XRF as it is a strong colorant and thus commonly present at low concentration levels while its Fe fluorescence radiation cannot be distinguished from that of earth pigments.

Co is present in areas having different tones of blue ranging from light blue to a more dark blue with a purple hue. This is not surprising since Co can be present as different pigments, namely as cobalt blue (CoAl$_2$O$_4$), as dark cobalt violet (Co$_3$(PO$_4$)$_2$) and light cobalt violet (Co$_3$(AsO$_4$)$_2$) and as cerulean blue (CoO·nSnO$_2$). Here, Co is generally correlated to Ni, which is not surprising as the two elements are often found in the same minerals; however, no correlation to As can be observed, excluding the use of light cobalt violet. A clear correlation between Co and Sn is strongly indicative of the use of cerulean blue for painting the flowers. In Figure 81, the pixels showing a strong correlation of this type are highlighted in green in the elemental distribution image of Co. The majority of the remaining Co is attributed to cobalt blue. While it is not possible to directly distinguish between dark cobalt violet and cobalt blue in these elemental distribution images (P and Al XRF signals were not detected by the mobile scanners under the chosen experimental conditions), one might suspect that both pigments were used for the creation of the blue flowers near points ‘c’ in Figure 81. However, dark cobalt violet has been found to be present in only six works of Vincent van Gogh and these were executed using a watercolour like technique. The pigment was observed to be correlated with Zn in these cases, which is not the case in this painting [1].

Cu and As (not shown) are found strongly correlated in the dark green areas, suggestive of the use of emerald green (Cu(C$_2$H$_3$O$_2$)$_2$·3Cu(AsO$_2$)$_2$).
The identification of Cr compounds is challenging as Cr may either be present in one or more green chromium(III) oxides (such as the darker viridian green, Cr$_2$O$_3$·2H$_2$O or the lighter chrome oxide green Cr$_2$O$_3$) or in one or more chromate pigments (M(II)CrO$_4$) of yellow-reddish colour when associated with different cations (e.g. M= Zn, Sr or Pb). These pigments have also been mixed by the manufacturer with other pigments to achieve completely different effects, such as green cinnabar, which has been described as a mixture of strontium chromate and Prussian blue. The same term has also been used to describe other pigment mixtures, such as lead chromate and Prussian blue [15]. While it is known that Van Gogh used a mixture of lead chromate and Prussian blue on a single occasion [1], the usage of a mixture of strontium chromate and Prussian blue has previously not been described.

In the Cr distribution image of Figure 81b, areas with a correlation between Pb and Cr are highlighted in red, suggesting the use of lead chromate. In other areas, a correlation of Cr with Sr and Ba is observed that is more difficult to explain. Sr and Ba sulfates may be present in different ratios as extenders in the paint, next to playing (albeit rarely) the role of counter ion in chromate salts. Fluctuations in the intensity ratio of Sr and Ba-L are observed, which is in good agreement with the results of Haswell et al. [2]. They observed variations in the Sr and Ba ratio within paint cross-sections prepared by FIB examined with SEM-EDX and TEM-EDX and explained these via the use of the mineral barite as source for Ba sulfate. In an attempt to distinguish between various Cr compounds and -species, the recorded Cr-K, Sr-K and Ba-L intensities were normalized and displayed in the ternary plot of Figure 81b. The vertical position in this plot is directly proportional to the measured Cr intensity.

The magenta coloured top area of the ternary plot (very high Cr intensity) corresponds to dark green areas in the painting where it is likely that viridian green was used.

The red area (high Sr signal) corresponds to areas, which may be related to the presence of strontium chromate, a yellow pigment; this appears to be consistent with the fact that many of these areas of the painting appear yellow is colour. However, there are some overlaps with the areas identified as lead chromates. The presence of strontium chromates could be confirmed by XRD analysis of a paint micro sample from a yellow area. However, not all areas with a high Sr signal are yellow, some are green. This indicates the use of green cinnabar, a mixture of Sr chromate and
Prussian blue. However, the usage of green cinnabar by Vincent van Gogh has never been described before and Prussian blue is, as discussed above, difficult to identify with XRF.

The yellow area in the ternary plot corresponds to pixels having a high Ba signal; these show a darker green tone than areas featuring a lower Ba content (indicated blue in the ternary diagram). We attribute this to the use of a green paint containing barium sulfate extender of different, possibly synthetic, origin.

Finally, the green and cyan part of the ternary plot features pixels with a higher Sr than Ba-L signal, also indicative of the use of a paint rich in Ba sulfate extenders. Both areas feature a similar Sr and Ba ratio but result from clearly separated areas of the painting. This can be caused either by the use of different mixtures of extender and Cr-based pigment or absorption effects, which attenuate the lower energetic Ba-L fluorescence radiation stronger than the higher energetic Sr radiation. It is also not possible to draw a clear border between the green and the blue zone, as natural fluctuations of measured values easily blend these areas together.

A close investigation of the Sb distribution shows that this element is present in those areas where SrCrO$_4$ and/or green cinnabar was used. Possibly Naples yellow was mixed in with the strontium chromate to add a yellow tone of the paint. The Cd map reveals on the other hand that cadmium yellow (CdS) was used independently to paint yellow highlights.

The observations made above could not have been obtained by XRF spot analysis, as it would have been difficult to determine if two elements are correlated in the same paint or present in superimposed layers or neighbouring features.

We could identify four yellow pigments (Naples yellow, cadmium yellow, strontium chromate and lead chromate), two red pigments (vermilion and minium), two blue pigments (cobalt blue and Cerulean blue) and at least two green pigments (emerald green, viridian green and possibly green cinnabar). Two pigments, Prussian blue and ultramarine were identified in a paint cross-section taken from the painting. This highlights that Van Gogh used this experimental painting to study the effect of different pigments and mixtures.

However, this section also shows the limitations of XRF for the identification of pigments throughout a large area on the surface of a painting. While MA-XRF can indicate the presence of a pigment, a definite
identification is not possible in all cases. Sometimes only assumptions can be made (e.g. green cinnabar) that have to be confirmed by other techniques, such as FT-IR, Raman, or by taking micro-samples from the painting.

This section was written with support by Ella Hendriks for [13] but not included in the final version of this paper due to page restrictions.
Figure 81a 40 x 40 cm sub-area of Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* as photograph and elemental distribution images. The areas indicated in green in the Cu image are correlated to Sn (see text). The upper part of the area was scanned by means of Instrument C (50 kV, 1.0 mA, 1 mm step size, 1.1 s/pixel), while in the lower part Instrument D was used (45 kV, 0.2 mA, 1 mm...
step size, 3.4 s/pixel). The scans were corrected for differences in sensitivity and dwell time before joining.

Figure 81b The areas indicated in red in the Cr image are correlated to Pb (see text). In the pseudo ternary plot the distance of a point from the upper corner is solely determined by its Cr intensity, while its horizontal position is determined by the Sr-K/Ba-L ratio.
4.6 References


Chapter 5 – NAAR: Comparison to MA-XRF
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4.7 Introduction

For a long time the only method to acquire distribution images with an element specific character in which underlying paint layers can be discerned was Neutron Activation Auto-Radiography (NAAR), first proposed by Sayre and Lechtman in 1968 [1]. In NAAR, transient radioactivity is induced in the painting by means of thermal or cold neutrons from a nuclear research reactor. After activation the painting is brought in contact with a photographic medium, photographic film or image plates, which are darkened by the emitted β-radiation. Differences in radioisotope half-lives allow for the acquisition of autoradiographs dominated by different elements; this is achieved by changing the photographic medium in appropriate time windows.
NAAR is a very suitable tool for the visualization of elements such as phosphorus (present in bone/ivory black, carbon-based black pigments containing a mixture of $\text{Ca}_3(\text{PO}_4)_2$, $\text{CaCO}_3$ and $\text{C}$, as a remnant of the animal bones burned during its production), manganese ($\text{Mn}$, present mainly in oxidized form in the earth pigment umber), copper ($\text{Cu}$, present in copper-based greens and blues) and mercury ($\text{Hg}$, present in vermilion $\text{HgS}$) due to their susceptibility to activation. Lead ($\text{Pb}$, present mainly in lead white) and iron ($\text{Fe}$, present in a broad range of pigments, among them earth pigments and Prussian blue) are upon neutron irradiation not transformed into radioactive equivalents that darken the photographic medium and cannot be imaged by this method. However, the distribution of $\text{Pb}$ is commonly well discernible in the XRR.

NAAR and MA-XRF differ considerably, not only in the fundamental physical phenomena exploited, but also in the way information is recorded. NAAR is a full-field technique that allows to investigate the entire surface of the painting simultaneously. MA-XRF, on the other hand, is a scanning technique and data is acquired in a sequential fashion. With NAAR, the intensity of the emitted $\beta$-radiation is "integrated" over a time window in the photographic medium, while in XRF the photons emitted are detected in an energy dispersive manner and the different element specific contributions to the XRF spectrum are separated during data processing. In NAAR the darkening of the photographic medium indicates the greater abundance of an element and no spectrometric figures-of-merit are obtained that can be compared to limits of detection calculated for XRF.

It is possible to obtain qualitative information about the elements present in a painting by recording the $\gamma$-radiation emitted after activation. This yields only local information for a number of spots on the surface of the painting, but supports the interpretation of the autoradiographs acquired.

As a scanning technique the lateral resolution of MA-XRF is determined by the size of the beam and the step size chosen. As mechanical constraints of a scanning system define a minimum dwell time per pixel, the time available for the experiment does not only affect the contrast obtained, but also the lateral resolution. In NAAR the contrast obtained is dependent on the exposure time of the photographic medium, which cannot be extended indefinitely to avoid overlap with slower decaying isotopes and overexposure in areas of high concentration. The lateral resolution of NAAR images is dependent on the grain size and thickness of the film employed and the distance between film and paint surface, which is influenced by the topography of the painting. Finally, the energy of the emitted $\beta$-radiation
influences the lateral resolution, as it determines the absorption in the photographic medium.

The main limitation of NAAR is that it requires the transport of the painting from the location it is normally exhibited in to the research reactor. Furthermore, after activation the painting needs to stay for several weeks at the reactor facility to acquire the autoradiographs and let the transient radioactivity fade below the legal limits. Due to the considerable financial and logistical effort of transporting the painting and removing it for prolonged time from the public, the number of paintings studied by NAAR is limited.

In this chapter the imaging capabilities of MA-XRF and NAAR will be compared in results obtained on Govert Flinck’s (1615-1660) Portrait of Rembrandt (see Figure 82). From XRR investigations of the painting it is known that in an intermediate stage the portrait showed the sitter without hat and with partly exposed forehead and ear. The attribution of the painting to Govert Flinck is controversial, not least on the basis of the similarity of the original composition to other self-portraits by Rembrandt [2].

Note: It is important to be aware of the difference in conventions between NAAR and elemental distribution images. In NAAR the darkening of the film is proportional to the amount of the element in question present. In elemental distribution images the brightness of a pixel is correlated to the intensity of the recorded fluorescence radiation.
4.8 Experimental

4.8.1 NAAR

The NAAR investigations were done at the BER II research reactor at the Helmholtz Zentrum Berlin (formerly the Hahn-Meitner-Institute) in November 1993. At this facility already the experiments described in [3-5] were performed. For activation the painting was placed on a motorized stage in a dedicated, climate controlled irradiation room. The neutrons leaving the reactor via a cold neutron guide of 3.5 x 12.5 cm² with an flux of 1.1 x 10⁹ cm⁻² s⁻¹ impinged on the surface of the painting under a shallow angle (<3°), so that a 12.5 cm broad stripe of the painting was irradiated simultaneously. By moving the painting vertically through the neutron beam the entire surface of the painting was activated for approximately three hours.

After activation, the painting was brought to a climate controlled dark room, where the photographic film was exposed to the β-radiation emitted from the painting. The schedule of film exposures, the radioisotopes dominating them and their respective half lives are given in Table 1. The NAAR measurements consisted of five exposures, each composed of four highly sensitive x-ray films that required the painting to stay at the reactor facility for two months. Between the first and second exposure the elements present in the painting were identified by recording γ-spectra from selected spots of the painting’s surface together with a longer measurement of the painting’s entire surface.

The goal of the NAAR experiments was the acquisition of high contrast images and not a precise identification of elemental distributions. Thus, no filters were used to separate the contributions of different elements, e.g. to remove the ⁶⁴Cu contributions in the first autoradiograph.
Table 8 Time windows and contributing radioisotopes of the autoradiographs. Half-life times are in brackets.

<table>
<thead>
<tr>
<th>Auto-radiograph</th>
<th>Time after activation</th>
<th>Duration</th>
<th>Strongly contributing radioisotopes</th>
<th>Weakly contributing radioisotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>17 m</td>
<td>2 h</td>
<td>$^{56}$Mn (2.6 h)</td>
<td>$^{64}$Cu (12.8 h)</td>
</tr>
<tr>
<td>02</td>
<td>6 h 42 m</td>
<td>18 h 30</td>
<td>$^{64}$Cu (12.8 h)</td>
<td>$^{76}$As (26.4 h)</td>
</tr>
<tr>
<td>03</td>
<td>1 d 4 h 14 m</td>
<td>1 d 20 h 30 m</td>
<td>$^{76}$As (26.4 h)</td>
<td>$^{64}$Cu (12.8 h), $^{197}$Hg (64.16 h)</td>
</tr>
<tr>
<td>04</td>
<td>3 d 4 h 12 m</td>
<td>4 d 30 m</td>
<td>$^{76}$As (26.4 h), $^{197}$Hg (64.16 h), $^{32}$P (14.3 d), $^{203}$Hg (46.6 d), $^{60}$Co (5.3 a)</td>
<td></td>
</tr>
<tr>
<td>05</td>
<td>7 d 5 h</td>
<td>45 d</td>
<td>$^{32}$P (14.3 d), $^{203}$Hg (46.6 d), $^{60}$Co (5.3 a)</td>
<td></td>
</tr>
</tbody>
</table>

4.8.2 MA-XRF

The painting was scanned with Instrument D with the 0.8 mm collimator to define the primary X-ray beam (see Chapter 2). Tube settings were 45 kV and 0.2 mA. The dwell time per pixel was 0.145 s with step sizes of 0.6 mm (horizontal) and 1.0 mm (vertical). The entire MA-XRF experiment took 16 hours.

For data processing the spectra acquired by the four detectors were scaled to the same energy and summed up. The spectra were processed with the PyMCA software package [6]. Correction of dwell time variations was done by post-processing the data. Elements up to Sn (Z=50) were primarily detected by their K-level fluorescence, while heavier elements were detected by their L- and M-level radiation.

The elemental distribution images obtained had a pixel size of 0.6x1.0 mm (h x v). To interpolate an apparent pixel size of 0.6x0.6 mm the images were stretched in vertical direction by an appropriate scaling factor.
4.9 Results

Figure 83 XRR and elemental distribution images of Pb-L, Pb-M and Ca. (XRR: Copyright Gemäldegallerie Berlin, Photographer: Christoph Schmidt.)

In Figure 83 the Pb distribution images obtained by MA-XRF are compared to the XRR. It is obvious that the map of the Pb-L lines gives comparable information but has reduced contribution from the support. In the XRR also a wax seal, probably coloured by vermilion, on the back of the painting is
clearly visible. The intermediate state of the portrait in that Rembrandt was shown without hat and with his forehead and right ear exposed is clearly discernible. Since the plume and the chain around his shoulder were executed in thick impasto with paint featuring a lower abundance of Pb these areas appear brighter in the XRR than in the Pb-L distribution image.

The lower energetic Pb-M radiation (~2.5 keV) is stronger absorbed in covering layers than the Pb-L radiation (Pb-L_α: 10.55 keV). So, when Pb-L and Pb-M distribution images are compared, it becomes clear that the Pb in the lit (right) part of the face is closer to the surface than in the shadowed region around the left eye. The shadow is also visible in the Ca distribution image and was probably applied as a thin glaze layer.

In Figure 84 the autoradiographs 01 and 02 are compared to the elemental distribution images of Mn and Cu. The Mn distribution is well recognizable in autoradiograph 01, especially in the shadowed part of the face and the pendant at the lower part of gorget, which is no longer visible in the final version of the painting. (The dark line in the lower left square is an artefact from handling of the photographic film during processing.) Next to Mn also Cu contributes to the image. While in the time window of autoradiography 01, Mn emits relatively more radiation than Cu, the higher abundance of Cu darkens the film, especially in the area of the plume.

The second autoradiography is dominated by Cu, but Mn still contributes slightly, while also Sn appears to do this (see below). The Cu distribution is dominated by material in the upper layers of the final portrait. Two Cu containing paint strokes are discernible on the gorget. While the right one coincides with the highlight set on the gorget below its rim, the left one is not connected to a discernible feature and was probably overpainted.

The Cu distribution image acquired by MA-XRF has been treated by histogram equalization, so that areas of large differences in intensity can be displayed in an 8-bit image file. This is possible due to the digital nature of the 32-bit elemental distribution images.

Histogram equalization could not be done on the autoradiography in a meaningful fashion. To allow for such a correction of the autoradiographs, photographs of them with a high dynamic range would be needed. Also autoradiographs acquired on image plates would feature a higher dynamic range.
Figure 84 Autoradiographs 01 and 02 and the elemental distribution images of Mn and Cu. The Cu distribution image was treated with histogram equalization to achieve a higher dynamic range. Note: The grey scale of autoradiographs and elemental distribution images are inverted; higher abundance results in autoradiographs in darkening of the film, while areas of intense fluorescence radiation in MA-XRF images appear as bright pixels.
Figure 85 Cu distribution image acquired by MA-XRF (left) and autoradiograph 03 (right). Note: The grey scale of autoradiographs and elemental distribution images are inverted; higher abundance results in autoradiographs in darkening of the film, while areas of intense fluorescence radiation in MA-XRF images appear as bright pixels.

In Figure 85 a detail of the Cu distribution image and autoradiography 03 of the plume is compared. The autoradiograph 03 also shows the Cu distribution and was chosen for this comparison as it features a better contrast than the slightly overexposed autoradiograph 02. Both images allow to follow the rough brush strokes of the plume, but only in the autoradiography the traces of individual hairs of the brush are visible.
Figure 86 Autoradiographs 03 and 05 and the elemental distribution images of Sn and Hg. Note: The grey scale of autoradiographs and elemental distribution images are inverted; higher abundance results in autoradiographs in darkening of the film, while areas of intense fluorescence radiation in MA-XRF images appear as bright pixels.

Autoradiograph 03 (see Figure 86) has the highest sensitivity for As, but as the presence of As can be excluded from the MA-XRF results it is still dominated by the same elements as autoradiography 02, with the exception
of $^{56}$Mn that has completely faded. In addition to these elements, also contributions from $^{197}$Hg are discernible.

At the beginning of the time window of autoradiograph 05, more than 20 times the radioactive half life of $^{64}$Cu had passed since the activation. The (integrated) contribution of $^{64}$Cu to this autoradiography is less than 1 ppm of the integrated contribution to autoradiograph 01 and 02. So the darkening in the area of the plume was not caused by $^{64}$Cu and can be attributed to $^{32}$P, which is assumed to be present in bone black. This pigment was mixed with the Cu-containing pigments. Under the chosen experimental conditions, Instrument D was not capable of detecting P. Co was neither by MA-XRF nor NAAR found to be present.

In the facial region, autoradiograph 05 and the Hg-L distribution are in good agreement. In both images additional details of the original painting are visible, such as the exposed ear and forehead. Areas of comparably low Hg abundance, such as the hair of Rembrandt are not well discernible in autoradiograph 05.

In autoradiographs 02, 03 and 05 a darkening of the film is observed that coincides with the distribution of Sn. Sn is present in the hatband and the chain on the shoulder of the final portrait. It is likely present in the form of lead tin yellow (type I: Pb$_2$SnO$_4$ or type II: PbSn$_{1-x}$Si$_x$O$_4$). This is a rather surprising observation, as Sn normally does not contribute to autoradiographs, since it is not highly susceptibility to activation. However, no other element that coincided with this darkening was found present by MA-XRF.

In this painting, lead tin yellow was applied in thick impasto, resulting in a high abundance of Sn. Furthermore, the impasto resulted in an uneven surface of the painting, so that the lead tin yellow containing paint was in direct contact with the photographic medium. These unusual and favourable conditions are assumed to cause the detection of Sn, probably via the decay of the $^{121}$Sn radioisotope (27.03 h) and possibly also via $^{113}$Sn (115 d).

Around the edge of the painting, a darkening of the film in autoradiographs 03 and 05 can be observed. This is attributed to minor amounts of Au leaf ($^{198}$Au, 2.69 d) from the frame of the painting that remaining on the surface during the NAAR investigation. Prior to the MA-XRF investigations, the painting was subjected to a conservation treatment and cleaned so that the minor amounts of Au were no longer present.
Figure 87 Fe distribution image, acquired by MA-XRF. The arrow marks a possible *pentimento* (see text).

In Figure 87 the Fe distribution image is shown; no equivalent distribution can be acquired by means of XRR or NAAR. Unsurprising, Fe is found all over the painting. Noteworthy are its presence in the facial shadows, probably in the pigment umber that also contains Mn and in the chain around Rembrandt’s shoulder. Here, Fe is assumed to be present in a yellow earth pigment.
In the Fe distribution, two *pentimenti* are visible. The arrow in Figure 87 marks a line that is not discernible in the visual photograph and that may indicate an intermediate position of the hat band. From the chain around Rembrandt’s shoulders, a pendant is hanging that is no longer visible in the final version of the portrait.
4.10 Conclusions

We have seen that both NAAR and MA-XRF are capable of revealing additional information about the *pentimenti* that were found in Govert Flinck’s *Portrait of Rembrandt* by means of XRR.

The elemental distribution images acquired by MA-XRF are more easily interpretable as they show all elements clearly separated. This is not the case in the autoradiographs that usually show a superposition of contributions from several elements. However, in combination with the γ-spectra that allow identifying the elements present on selected spots of the surface, the distribution of elements can be largely deduced from them.

MA-XRF is sensitive to a broad range of elements, while NAAR is sensitive to only a limited number of these (Mn, Cu, Hg, As, P, Au and probably Sn); this is determined by the susceptibility of these elements for neutron activation and by the decay times of the resulting radioisotopes. It is worth mentioning that under the commonly employed experimental conditions for MA-XRF (detector settings, distance between detector and sample, X-ray tube settings) Instrument D is not capable of detecting P. However, the M6 Jetstream features a better sensitivity for P and could already in several studies be used to acquire (noisy) P distribution images. The investigation of P by MA-XRF is limited to the surface layers, as the low energy fluorescence radiation (P-K$_\alpha$= 2.0 keV) is absorbed in covering layers.

In the comparison of autoradiograph 05 and the Hg-L distribution image, areas with a relatively low abundance of Hg, such as the hair of Rembrandt, are not directly discernible in the autoradiograph. This is mainly attributed to the fact that in MA-XRF, the spectral background and the net elemental signals can be separated during data processing and thus lower limits of detection are achieved.

MA-XRF is considerably more surface sensitive than NAAR. Most signals recorded in the MA-XRF experiments (with the exception of Sn-K) had an energy below 20 keV and more than 95% of this radiation would have been absorbed in a 50 µm thick Pb foil. Sayre and Lechtman found that such a foil would only stop β-radiation with an energy of less than 0.3 MeV, so that most elements detected by NAAR in this project would be only attenuated. Notably, $^{203}$Hg features β-radiation with an energy below this threshold and thus its β-radiation would probably no longer cause a darkening of the film.

The autoradiographs presented in this chapter feature a higher lateral resolution than the elemental distribution images acquired by MA-XRF. This is mainly due to the limited time available for the XRF scan. Instrument C and the M6 Jetstream are both able to record elemental distribution images
with a lateral resolution of less than 100 μm, provided sufficient time for the experiment is available. However, as discussed in Chapter 2, such an investigation would require a constant distance between the measurement head and the surface of the painting; in practice this requirement would limit the subareas that can be investigated to a few tens of square centimetres.

The available autoradiograph images are digital photographs of the original autoradiographs; these feature a limited (8-bit) dynamic range. Elemental distribution images are acquired in a digital fashion and commonly saved as 32-bit floating point data sets. Thus, histogram equalization and other image processing techniques can be applied on them with more success than on autoradiographs.

As data of all elements is recorded simultaneously in MA-XRF, the various distribution images are perfectly aligned for comparison. This is not the case for the autoradiographs and the alignment needs to be done manually in a post processing phase. On the other hand, autoradiographs are 1:1 reproductions of the painting, while elemental distribution images need to be manually scaled.

In addition to the fact that MA-XRF makes it possible to study the distribution of Fe, which is not possible by NAAR and XR, the main advantage of MA-XRF is considered to be its flexibility. A NAAR investigation cannot be accelerated, while in case of MA-XRF a larger step size and/or shorter dwell time can be chosen to reduce the total measurement time required. Since no transport of the painting outside the museum is necessary, the financial and logistical effort for the investigation of a painting is considerably reduced.

This comparison has to be seen in the light that the NAAR investigations were done 19 years prior to the MA-XRF experiments. Since this investigation, the use of image plates was introduced for NAAR data acquisition (in parallel with the use of X-ray films). The more sensitive image plates allow for shorter exposure times and thus lead to a reduced mutual interference among the radioisotopes; they also provide digital images of a higher dynamic range than digital photographs of X-ray films. However, the lateral resolution of NAAR data obtained with image plates is inferior to that recorded on X-ray films. NAAR images acquired by image plates also need to be carefully aligned for comparison with other images.

It is expected that if mobile MA-XRF instruments become more widely available, MA-XRF will largely replace NAAR. NAAR will probably be limited to cases where P (bone black) in covered layers is of interest or the hidden
composition is covered by strongly absorbing paint so that many useful XRF signals from hidden layers cannot escape from the painting.

The NAAR results were provided by Claudia Laurenze-Landsberg of the Gemäldegalerie Berlin, Germany.
4.11 References


5 Conclusions and Perspective

5.1 Conclusions

Historical paintings can be considered as one of the most precious parts of humanity’s cultural heritage. Their investigation and preservation for coming generations is supported by scientific investigations. Paintings have a layered structure that is created in a sequential fashion by applying paint layers on the prepared ground and on top of one another. Especially the layers present below the surface often contain information on the *modus operandi* of the artist and remnants of the painting’s original concept (*pentimenti*). This information can be highly relevant in discussions on the authorship of the paintings. Paint is opaque to visible light so that covered layers are not discernible with the bare eye; scientific techniques are therefore required for their study.

A broad range of methods has been used or proposed for the study of covered paint layers in recent years. This is rather unsurprising, as the investigation of historical paintings and cultural heritage in general is of interest not only to a small group of experts, but also to the general public. Nevertheless, only a small number of research centres next to individual research groups are actively pursuing their research in this field and, consequently, the investigation of historical paintings is not an attractive market for the manufacturers of scientific instruments.

Most instruments that are currently employed were designed for other applications, not the inspection of historical painting and were often modified to increase their applicability. For example, the development of X-ray radiography instrumentation has been driven by the needs of industrial and medical imaging; its use was afterwards adopted by conservation studios.

Before the introduction of scanning macro-XRF (MA-XRF), the chemical elements present in paintings could only be determined locally, either by sampling the painting and preparing a cross section through the paint stratigraphy for investigation with SEM-EDX or by investigating a number of locations in a non-destructive manner with a portable XRF instrument. A method that provides information comparable to MA-XRF is multi-spectral imaging; it allows for the acquisition of distribution images with a chemical contrast. The capabilities of this technique to identify the
pigments used are limited to those of which reference spectra are available and are present at the surface.

The only other method that allows for the acquisition of images with an element specific character is Neutron Activation Autoradiography (NAAR). In this method transient radioactivity is induced in the painting by means of neutrons from a nuclear research reactor. After activation, the painting is covered with a photographic medium (usually X-ray film). This medium is exchanged in selected time windows. By exploiting differences in the half life of the transient radioisotopes, autoradiographs are acquired that feature elemental contrast but in which the various elemental contributions are often not clearly separated. Furthermore, NAAR requires the painting to stay for several weeks at the reactor facility for the acquisition of the autoradiographs and letting the induced radioactivity fade below the legal limit. For this reason and the need to transport the painting to the research reactor, the number of paintings that can be investigated by NAAR is limited.

In this work, instrumentation for MA-XRF was developed and employed for the investigation of historical paintings. MA-XRF fills a gap in the array of methods available for the investigation of historical paintings, as it allows to acquire elemental distribution images of large areas (up to several square metres). In MA-XRF a focused or collimated X-ray beam of typically a few tens to a few hundred micrometres diameter is used to scan the surface of the painting. The fluorescence radiation that is emitted by the painting upon irradiation is recorded by one or more energy dispersive detectors. Elemental distribution images are obtained by setting each pixel to a grey scale value corresponding to the intensity of the recorded fluorescence radiation. Due to the penetrative nature of X-rays, elemental distribution images allow to study the distribution of elements in the surface and sub-surface layers of a painting.

The first MA-XRF experiments were done at the synchrotron radiation (SR) sources DESY (Hamburg, Germany) and NSLS (NY, USA); this necessitated the transport of the paintings to these SR facilities. Due to this and the limited availability of beam time, only a small number of paintings could be investigated there. In order to circumvent this limitation, in parallel to improving the synchrotron based scanners, on an explorative basis, Instrument A was built by re-configuring an existing micro-XRF instrument into a mobile macro-XRF scanner.

While the capabilities of this scanner were limited to scanning less than 10 pixels per minute, this instrument allowed us to show that it was
feasible to obtain good quality elemental distribution images of historical paintings by means of X-ray tube based MA-XRF apparatus.

Instrument A was improved in several steps by integrating motor stages with a larger travel range, more powerful X-ray tubes and multiple detectors, yielding Instruments B to D. The two most recent instruments employ a motorized stage with a maximum travel range of 60x60 cm$^2$ and four silicon-drift-detectors (SDDs). Instrument C features a 50 W Mo-Anode X-ray tube with a fixed polycapillary X-ray lens, featuring a minimum beam size of approximately 50 µm. In Instrument C the detectors record fluorescence radiation from four different angles. Instrument D features a 10 W Rh-anode X-ray tube and a pinhole collimator as beam defining optic, yielding a minimum beam size of 600 µm. The more efficient detection geometry and the pinhole collimator of Instrument D allow recording fluorescence radiation with more than five times the sensitivity of Instrument C. Especially for elements heavier than Cd, which are difficult to detect by Instrument C, Instrument D features roughly 100 times the sensitivity. Both instruments are capable of scanning an area of 60x60 cm$^2$ with a step size of 1 mm in 20 hours and acquire noise-free elemental distribution images of elements correlated to the main components.

The results acquired by the in-house built scanners found general acceptance in the painting conservation and art-historical community. Thus Bruker Nano GmbH (Berlin, Germany) decided to build a commercially MA-XRF scanner for the investigation of large, planar objects. The instrument was based on the technical know-how of Bruker Nano GmbH in the design of XRF scanners and the experience obtained with the in-house built scanners of the University of Antwerp. The instrument, baptized M6 Jetstream, features spectrometric figures-of-merit comparable to that of the in-house built scanners. Due to its more efficient control software, it allows for the acquisition of more than 100 pixels/s.

The figures-of-merit of SR based instruments in general surpass that of X-ray tube based scanners. However, the difference in performance is in general not so large that it would justify the transport of paintings to a SR facility; the lower absolute levels of sensitivity of the mobile scanners relative to those at synchrotron facilities can be largely compensated by longer measurement times.

Until a few years ago, XRF imaging was performed on small areas by acquiring a few (ten)thousands of spectra. These data sets were
processed by least squares fitting of individual spectra in software packages such as AXIL and PyMCA. Technical progress in the fields of X-ray sources, optics and detectors continuously enhances the pace of data acquisition in XRF scanning. Especially in the case of historical paintings, where the elements of interest are present at concentration levels of several mass percent, dwell times of fractions of a second per pixel are possible, yielding data sets of hundred thousands to millions of pixels/spectra.

While initially the data acquired on historical paintings was processed with AXIL and PyMCA, the higher pace of scanning made it impractical to continue using these packages as - under favourable circumstances – data could be acquired faster than it could be processed. The timely evaluation of a data set is desirable, as it allows considering the results of previous experiments when planning the following. To accelerate the data processing, a software package (called Datamuncher) was written. Next to scheduling batch least squares fits with aforementioned software packages and allowing for an export of elemental distribution images to common graphic formats, the Datamuncher package allows for the processing of several thousand spectra per second based on Dynamic Analysis (DA).

In DA the spectrum, or an array of spectra, is multiplied with the DA matrix. The DA matrix contains shapes derived from the elemental profiles obtained in a least squares fit of the sum of all spectra in the data set. Via the shapes of the DA matrix, interference between elemental lines and other features is taken into account. Matrix multiplication is a fast operation on a computer and DA allows processing of several thousands of spectra per second.

DA was developed for the proprietary GeoPIXE software package, which only became available in the last year of this work. DA, as it is included in GeoPIXE, assumes the shape of the spectral background to be constant. An assumption that is valid in many, but not in all cases. To compensate for differences in background shape in the Datamuncher two approaches were followed: either the shape of the spectral background was estimated by the SNIP method and subtracted prior to the data processing or it was included in the DA matrix in the form of linear polynomials. In most cases, the use of linear polynomials was found sufficient to acquire elemental distribution images without artefacts from the shape of the spectral background.
Furthermore, it was shown that elements present in low abundance in a fraction of the scanned area can be better identified in a spectrum composed of the maximum intensity of each channel in the entire data set, instead of a sum spectrum of it.

Many elemental distribution images acquired on historical paintings contain artefacts, resulting from the absorption of signals emitted from hidden layers in covering ones. While on the one hand, these artefacts can render the distribution images difficult to read, on the other hand they contain information on the stratigraphy of the painting.

By means of the data set acquired from Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* at the DESY synchrotron, it could be shown how absorption artefacts can be corrected for based on fundamental parameter calculations.

Furthermore, it was investigated in how far these artefacts can be exploited to gain insight into a painting’s stratigraphy and to distinguish between surface and sub-surface layers. For this, the intensity ratio of fluorescence lines of different energies or recorded under different detection angles was used. Such data can be acquired by means of Instrument C and the DESY scanner. While the results obtained often gave complimentary information to elemental distribution images, it was difficult to distinguish between absorption effects in covering layers and due to self-absorption. Thus, great care needs to be taken in the investigation of a painting’s stratigraphy by MA-XRF.

MA-XRF allows for the investigation of a wide range of questions in historical paintings, as could be demonstrated in several case studies.

The method is well suited to obtain additional information on discarded and overpainted works, whose presence could be detected by X-ray radiography, but of which the pictorial details could not be identified. This was achieved in case of Vincent van Gogh’s *Birds’ Nests* and Francisco de Goya’s *Portrait of Ramón Satué*.

In case of *Birds’ Nests*, the hidden composition could be identified as a fragment of a painting depicting a farmer with an oxcart, possibly in winter. Under the *Portrait of Ramón Satué*, a second portrait by Goya is present. While the sitter’s identity could not be revealed, it was possible to identify his uniform as that of a highly decorated general of the army of Joseph Bonaparte, King of Spain.
Pentimenti in historical paintings can give insight in the artists’ original intention. This was illustrated in two case studies: In *Pauline im weißen Kleide vor sommerlicher Baumlandschaft*, which is controversially attributed to Philipp Otto Runge and Caravaggio’s *Rest on the Flight into Egypt*. In case of *Pauline* it could be revealed that the sitter was originally depicted in a more revealing dress, with open hair and hair bands. In the *Rest on the Flight into Egypt* the repositioning of Mary could be shown.

In two cases it was possible to support the attribution of a painting to an artist. The authorship of Rembrandt van Rijn could be confirmed in case of *Portrait of an Old Man* by visualizing the sketch for an unfinished self-portrait by Rembrandt under the surface. In case of *Flower Still Life with Meadow Flowers and Roses* the MA-XRF investigation could provide sufficient information on the underlying composition of two wrestlers to link them to Van Gogh’s oeuvre and letters.

MA-XRF can also support the distinction between original paint and retouches. This information is of great value in the planning of conservation treatments, as the latter may be removed, while the first needs to be preserved. This was illustrated with the examples of Rembrandt van Rijn’s *Saul and David* and the *Portrait of Engelbert II*.

Also the pigment use of an artist can be studied in elemental distribution images. This allows for in detail investigations beyond what is possible by spot analysis by means of portable XRF. This was illustrated in a case study of Vincent van Gogh’s *Flower Still Life with Meadow Flowers and Roses* and in case of four paintings by Caravaggio.

In a final case study a direct comparison of NAAR and MA-XRF was possible on Govert Flinck’s *Portrait of Rembrandt*. It was found that autoradiographs feature a higher resolution than commonly achieved in MA-XRF experiments. Furthermore, NAAR features a higher sensitivity for P, which is in general only weakly detected by MA-XRF in surface layers.

MA-XRF, on the other hand, allows for a faster investigation of historical paintings without the need to transport them from the museum to a research facility. It is sensitive to a broader range of elements, most prominently Fe. However, since it is more surface sensitive than NAAR, elements present in thickly covered paint layers are less visible in elemental distribution images acquired by MA-XRF.

This work has made a valuable contribution to the range of methods available for the investigation of historical paintings. The instrumentation
available for MA-XRF investigation has progressed in less than 5 years from highly experimental set-ups at SR facilities over in-house built scanners to mature and commercially available dedicated instruments.

5.2 Perspective
A general perspective for the investigation of historical paintings is difficult to draw, as the investigation of cultural heritage artefacts is in economic troublesome times often considered a non-vital field and might be subjects to funding cuts. However, most investigations are done by means of complimentary in-situ techniques. New instrumentation will, as it is now, mainly be adapted from other fields, such as the medical field and non-destructive testing.

MA-XRF is expected to play an important role in the investigation of historical paintings, provided mature instruments are available. The instruments presented in this work might also be used for the investigation of other large, planar pieces of cultural heritage, such as stained glass and historical manuscripts. They might also find application in the investigation of large fossils.

MA-XRF has two fundamental limitations: it only offers elemental, not chemical contrast and self-absorption effects render the detection of light elements in covered layers challenging. Furthermore, the elemental distribution images obtained with MA-XRF are 2-dimensional projections with only limited depth information.

These limitations can be overcome by combing MA-XRF with complimentary techniques. Imaging techniques can be used to re-investigate the entire scanned area or investigate sub-areas of special interest identified in the larger elemental distribution images obtained by MA-XRF. Also the analysis of a limited number of spots can support the interpretation elemental distribution images.

Techniques suitable for the identification of pigments are FT-IR spectrometry, micro-XRD (imaging) and XANES. Especially micro-XRD is less hindered by absorption effects than XRF. Furthermore, MA-XRF may be combined with optical coherence tomography (OCT) and computed laminography for depth profiling. If THz spectroscopy matures and is extended towards higher frequencies, it may serve for both purposes. A combination of such techniques in one measurement head for parallel usage would be desirable, but is technically challenging, not the least due to geometrical and weight constraints of the motorized stages.
The most recent MA-XRF instruments presented in this work can be considered mature. In "XRF-only" MA-XRF instrumentation, only minor improvements are expected, such as the use of collimator optics for the M6 Jetstream to enhance its sensitivity for heavier elements (such as Cd, Sn and Sb). Advanced XRF detectors could be integrated in MA-XRF instruments to enhance the sensitivity. However, this would require a significant engineering and financial effort, which would not be necessarily matched by the gain in performance. The control software of the scanners is expected to evolve, allowing for the faster and artefact free acquisition of elemental distribution images.

While for the large scale XRF scanning of paintings, the use SR facilities does not appear to include any advantage other than that of speed, some techniques complimenting XRF benefit much more from the characteristics of SR than MA-XRF itself, notably micro-XRD. XANES and computed laminography are commonly limited to SR facilities.

In order to enhance the depth sensitivity of MA-XRF, two approaches are possible. On the one hand, an instrument might combine two detectors at gazing exit geometry and normal geometry. However, such an instrument would be less sensitive than one with a conventional detection geometry and might suffer from geometrical constraints.

On the other hand, confocal XRF might be used for the acquisition of depth profiles. X-ray tube based instruments are currently limited to dwell times of several tens of seconds per point, limiting the method to the investigation of a few spots. At SR facilities, dwell times in the range of one second can be achieved so that the investigation of (small) 3-dimensional volumes is possible. Like other depth profiling techniques confocal-XRF can support the interpretation of absorption exponent and line ratio maps. In how far imaging detectors, such as energy dispersive X-ray cameras, accelerate data acquisition in case of confocal XRF for historical paintings remains to be explored.

All these instruments will benefit from the general evolution in X-ray detector, optic and source technology.

In terms of data processing it has been shown that Dynamic Analysis is better suited for the evaluation of large XRF data sets than least squares fitting of individual spectra. As the progress in X-ray optics, sources and detectors allows for an ever faster acquisition of XRF data sets, it is expected that DA will find wider usage in the near future than in the last
decades, also because it is planned to be integrated in the PyMCA software package and so no longer limited to GeoPIXE.

Historical paintings are complex samples, with a considerable content of “dark matrix” so that the development of a general model for the removal of absorption artefacts from the acquired elemental distribution images can be considered as challenging. However, the presented calculations can serve as an example for future correction of absorption artefacts.

A quantitative interpretation of the acquired XRF spectra would support the depth discrimination, as it might be used to validate the results obtained and support the interpretation of line ratio and absorption exponent maps. But also this approach is of limited use for complex samples, for example in those cases where the same element is present in several layers.