

# De Mayerne PROGRAMME

NWO research  
programme on  
molecular studies  
in conservation  
and technical  
studies in art  
history

# Working methods of the old masters

Detail of red garment with discoloured vermilion - PHOTO SRAL

The De Mayerne programme for the 2001-2006 period is an NWO research programme on molecular studies in conservation and technical studies in art history. In the first round, which took place in 2001, grants were awarded to five projects. A second round is due in autumn 2002. For more information visit the NWO website: [www.nwo.nl](http://www.nwo.nl).

COVER PHOTO Thomas Willeboirts Bosschaert, detail from Frederik Hendrik and Maurits as commanders, with in the distance the battle at Nieuwpoort, ca. 1650 - PHOTO SRAL



## MODERN TECHNOLOGY REVEALS WORKING METHODS OF THE OLD MASTERS

The aim of NWO's De Mayerne research programme is to advance knowledge of the process of ageing in the layers of paint and varnish found in paintings dating from the early 15<sup>th</sup> to the close of the 19<sup>th</sup> century. Investigation of the practices of painters and the way paintings were physically created is expected to cast light on problems of art history and restorative treatment relating to the cultural heritage of the Netherlands. This will eventually enable the establishment of a theoretical framework for the improvement of action to preserve and restore works of art. The multidisciplinary programme involves close cooperation between analytical chemists, physicists, restorers and art historians. De Mayerne is a sequel to NWO's MOLART (Molecular Aspects of Ageing in Art) research programme.

The De Mayerne research programme is being implemented in close cooperation with a number of museums in the Netherlands, including the Mauritshuis, the Rijksmuseum and the Van Gogh Museum. Projects are based on the problems, expertise and experience of restorers and art historians and focus on the paintings in the collections of these museums. Other bodies directly involved in the programme are the FOM Institute for Atomic and Molecular Physics (AMOLF), which amassed vast expertise in this area during the MOLART programme, and the research department of the Netherlands Institute for Cultural Heritage (ICN). The latter will also contribute to the wide dissemination of the knowledge and experience generated

by the programme. There is also close cooperation with specialists at foreign institutions, such as the Tate Gallery in London.

The De Mayerne research programme now encompasses five closely interrelated research projects. This brochure contains a brief description of each of them. A major factor in all the projects is the impact both of the restorative treatment accorded to the paintings in the past and of the natural process of ageing. The results of the research conducted within the De Mayerne programme will in turn have major consequences for future restorative treatments and restorations and for action to optimise the conditions in which works of art are preserved. The five projects will provide a sound basis for the further expansion of the programme. It is desirable that broader-based research should eventually gain a place within it, for example the effect of solvent use during restoration work, or the working methods of painters in the Golden Age. Multidisciplinary cooperation is a precondition of success in all parts of the programme. The MOLART programme has shown that this is possible and I am certain that the De Mayerne programme will help to intensify the cooperative partnerships that already exist.

**Dr. J.P. Filedt Kok** (Chair De Mayerne Programme Committee; keeper of paintings Rijksmuseum)



## MOLART: MOLECULAR ASPECTS OF AGEING IN ART

### Who was De Mayerne?

Sir Theodore Turquet de Mayerne (1573-1655) moved in 1611 from France to London to become principal physician to James I. At the English court he carried out research on technical aspects of painting and performed chemical experiments, leading to the discovery of a purple pigment for enamel painting. The results of his studies are contained in *Pictoria sculptoria et quae subalternarum artium*. In this manuscript, De Mayerne presented many recipes and instructions, derived from miscellaneous sources like old treatises on painting techniques. However, his main source of information was formed by the many conversations he had with artists, including Rubens, Daniel Mijtens and Anthony van Dyck. De Mayerne's manuscript still is used as one of the main sources on 17<sup>th</sup> century painting techniques.

MOLART was a recognisance research programme for the molecular study of art objects, especially paintings. It achieved an increased awareness of the potential of the molecular approach for the understanding of complex phenomena and demonstrated that paintings are not static objects but dynamic systems that still respond physically and chemically to environmental processes even after hundreds of years. Access provided under MOLART to new techniques at the FOM Institute for Atomic and Molecular Physics (AMOLF) provided insight into the molecular level by linking microscopy, spectroscopy, mass spectrometry and advanced data processing methods to examine the composition and distribution of organic and inorganic components in paintings. Reports on research conducted under MOLART are published as PhD theses (MOLART Report Series) and as research papers in the public domain.

MOLART was an NWO Priority Programme. This implied that the scientific value of the output had to be matched by the social relevance of the results. The value to society of studies concerning the preservation of our cultural heritage is obvious to everyone. Nobody wants to lose the precious art collections created and bequeathed by our ancestors. MOLART team members participated in the research and conservation programmes of museums in the Netherlands and abroad. Knowledge was transferred directly to students of conservation via various teaching programmes and also to the general public via radio and TV shows,

newspaper articles and exhibitions. The policy of complete openness about the projects, the early transfer of knowledge and the exchange of ideas made MOLART and its team a recognised partner to the international art conservation community. MOLART was represented at many international conferences on conservation and other meetings of scientists, where team members gave oral presentations, presented papers and displayed posters about the programme (listed at [www.amolf.nl](http://www.amolf.nl) under MOLART).

#### **MOLART > The De Mayerne Programme**

In many ways, the De Mayerne Programme builds on the ideas and concepts developed during the MOLART Programme. The idea of bringing art historians, research restorers and scientists together in one team has been continued and more firmly established by the appointment of coordinating principal investigators (CPI). There is an acute awareness of the necessity to cooperate in a multi-disciplinary way to tackle the complex problems of the interaction of painting materials in multi-layer systems studied in a historically accurate context. The De Mayerne projects are nurturing a formula for collaboration that was developed during MOLART, which will keep the MOLART approach and spirit alive.

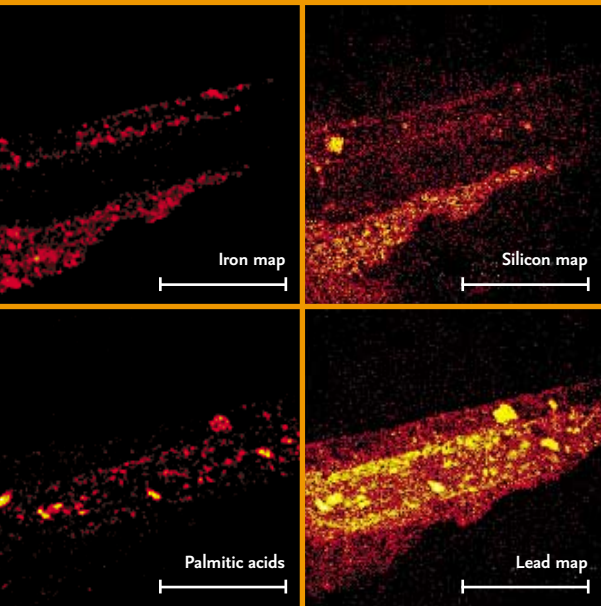
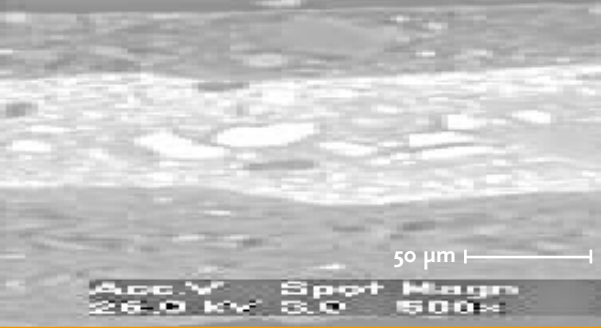
**Prof. dr. J.J. Boon**

(MOLART Studies Group, FOM Institute AMOLF)

# Paint cross-sections



## IMAGING MICROSCOPY OF PAINT CROSS-SECTIONS



Cross-sections describe the depth dimension of paintings. The superposition of layers, the layer thickness, the grain size, the kind of pigment and the binding medium are important microscopic properties which mark the technique of a painter. A paint cross-section gives an in-depth view of the painting process and can reveal what happened while the painting was ageing to its present state. The aim of the Molecular Mapping of Paint Cross-Sections (MOLMAP) project is to continue the development of microscopic-spectroscopic and microscopic-mass spectrometric research methods for cross-sections that will image the spatial distribution of organic binding media and pigments. Such research is of vital importance to technical studies in art history, studies of processes of chemical change in paintings and studies concerning the effects of conservation methods.

MOLMAP is intricately linked to the other projects funded under the De Mayerne Programme.

Its methodology supports studies on:

- › The paintings in the Oranjezaal,
- › Paint media deterioration in paintings by Van Gogh,
- › The role of lead coordination in oil paint stability,
- › The process by which oil paint changes into a stable ionomeric network,

- › The investigation of destructive processes of chemical change in oil paints leading to erupting protrusions, transparent inclusions, colour changes and increased transparency.

MOLMAP's mission is to determine the spatial distribution of binding media, resins and inorganic materials in the multilayer system of paintings. Its central research issue concerns the nature of the interactions between these materials as a function of time. Paintings are much more dynamic than previously thought. Study of the process by which oil paint changes from a plastic oil-derived network polymer to a brittle ionically bound ionomeric polymer system as paintings age, has made us aware that metal organic interactions are the key to understanding how a painting will respond to environmental conditions and conservation treatment. MOLMAP will apply imaging methods to investigate the nature of these interactions in paintings.

Severe forms of deterioration of paint layers have been detected in a number of 17<sup>th</sup> century paintings by Hals, Vermeer, Steen, Rembrandt and others, and in 19<sup>th</sup> century paintings by Van Gogh and his contemporaries. These deformations are related to dynamic chemical processes in the paint and are partially determined by



## THE COORDINATION CHEMISTRY OF LEAD AND CHEMICAL CHANGES IN AGEING OIL PAINTINGS

processes occurring at the interface of mineral surfaces of the pigments and components of the binding media. The MOLMAP team has plans to collaborate with other project leaders within the De Mayerne Programme in an effort to increase understanding of these processes. High-resolution chemical imaging maps on the distribution of the oil paint binding media components obtained by way of imaging secondary ion mass spectrometry (SIMS), imaging FTIR and SEM-EDX will be correlated with material features and technical knowledge of painting and paint formulation. These imaging studies will support the study of the history of painting and the study of painting materials. Several studies of specific paintings are planned with the participating museums and as part of an open-laboratory agreement benefiting both the MOLART Studies Group at AMOLF and the Conservation Department of the Mauritshuis.

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### Participating institutions

AMOLF, Mauritshuis, Van Gogh Museum, SRAL, Leiden University, Rijksmuseum, ICN, Tate Gallery

**CPI: Prof. dr. J.J. Boon** (FOM Institute AMOLF)



# Chemistry of lead and chemical changes

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This project concerns the use of theoretical and experimental studies on the coordination chemistry in paint layers to explain changes in the paint chemistry of ageing paintings. Paintings are highly composite materials. Even after centuries, many chemical processes still continue. The chemical reactions start during the production of binders, such as linseed oil, or alkyd resins in the case of modern paints. Next come pigments, solvents and many other special components. The various processes that occur during the mixing of the paint, its application, the drying processes and subsequent ageing are both physical and chemical. Physical processes include the emulsifying of the paint during its production, the evaporation of solvents during drying and the simultaneous diffusion of oxygen into the paint layers. Among the many chemical processes are the anti-skinning action for paint still stored in its container, the polymerisation of the binder after application and the chemical ageing processes that take place over the subsequent lifetime of the painting.

Nowadays it is well known that coordination chemical processes play highly important roles in all aspects of life. For example, the respiration process of many living creatures starts with the uptake of oxygen from air by an iron atom present in haemoglobin. >>>

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As paint dries, oxygen reacts with the binder producing a polymeric network which constitutes the paint layer. This reaction is catalysed by metal compounds present in the paint mixture. In modern paints these catalysts may be manganese, iron or cobalt compounds, and such catalysts are added on purpose. In traditional paints used by artists, the function of catalysts was exerted by the metal compounds that were present as pigments. Quite a number of pigments contained iron, manganese, cobalt, copper, chromium, mercury, arsenic, chromium or lead. Of all these, lead is the most important as it is the basic metal component of lead white, which is an omnipresent component in paintings of the last four centuries.

It has recently been established that lead white particles may react during the ageing process of the paint with aged oil paint binding material to produce lead carboxylates, which are not brilliant white pigments like lead white itself and do not have the same physical properties. The result is the appearance of small craters filled with a dull white material, in which even orange coloured minium particles can occur, probably formed by some subsequent autoxidation process. Coordination chemists want to understand why such processes can occur and what compounds tend to be formed from

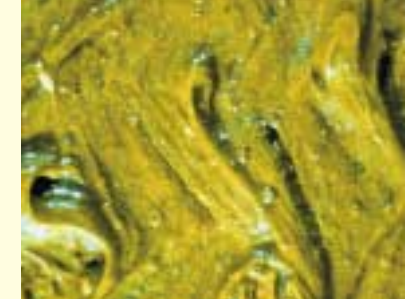
what kind of lead whites and under what circumstances. Other lead-containing pigmented oil paints like lead-tin yellow paint can also display such changes. It remains unclear what causes them. To investigate this behaviour of lead, a chemist needs input from micro-analyses on the paintings. Model compounds are then synthesised to compare with the micro-analytical results. For recognition of the many solid state phases in which the lead ions may exist, X-ray powder diffraction can be used. A relatively new technique that will be used is  $^{207}\text{Pb}$ -nmr on solid state samples. This technique is very sensitive in distinguishing lead in different coordination chemical environments.

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### Participating institutions

Leiden University, AMOLF, Van Gogh Museum, Mauritshuis, Rijksmuseum, ICN, SRAL

**CPI: Dr. J. Haasnoot** (Leiden University)



Self-portrait as a painter, Vincent van Gogh,  
© Van Gogh Museum, Amsterdam



# Materials & technique of Van Gogh



## THE PAINTING MATERIALS AND TECHNIQUE OF VINCENT VAN GOGH



There is a general dearth of information regarding painters' practice in the late 19<sup>th</sup> century, when the last traces of traditional studio practice were disappearing and the use of mass-produced materials were becoming the norm. The work of Van Gogh may illustrate this development, demonstrating some pitfalls arising from early tube paint formulations as well as a largely self-taught technique. Moreover, an in-depth investigation of Van Gogh's painting materials is directly relevant to his French contemporaries, including the Impressionists, Gauguin, Seurat and Signac, all of whom are known to have obtained materials from the same source as Van Gogh at some point in time.

Roughly 40% of Van Gogh's known works are preserved in the Netherlands, providing a unique research resource. In addition, the Van Gogh Museum houses around 800 of Van Gogh's letters to his brother Theo, containing a wealth of information about his creative processes and the methods and materials he used. Technique was an area of constant experiment for Van Gogh and the way he painted is intimately linked to the meaning of his pictures. Hence, technical research brings us closer to his work by helping us to understand how his pictures were made, how they may have looked originally, and why they look the way they do now.

A prime objective of this project within the De Mayerne programme is to identify aged materials present in Van Gogh's paintings and study their distribution there. Special attention will be devoted to the investigation of typical degradation phenomena. These paint defects have often dramatically altered the pictorial image and at the same time imposed limitations on possible treatment and methods of display. Examples include the migration of lower paint layers up through cracks when in a plastic state, the formation of transparent globular protrusions in certain areas of colour, the soft and powdery consistency of particular paints, and the tendency of certain synthetic and natural organic red paints to fade or change colour.

A second focus of the project will be to investigate how Van Gogh was able to manipulate the consistency of his paint to achieve different painterly effects. It will examine the relationship between the rheology of his brushwork and the ready-to-use formulation of his tube paints. It will also investigate the possibility that he modified the working properties of his paints by adding other media on the palette. Historically accurate reconstructions of Van Gogh's paint composites will be made in order to try to emulate the flow properties of his paint by varying certain characteristics. >>>

# Historically accurate

# recon- structions



HISTORICALLY ACC

A third aspect of the project relates to issues of dating and attribution in Van Gogh's oeuvre. Until recently, technical examination and analysis of his paintings played only a very limited role in this discussion. The usefulness of technical information was often questioned, given that the artist used materials that were manufactured on a commercial scale and were generally available at the time. Focussing upon Van Gogh's well-documented production in Saint-Rémy and Auvers, pilot studies will be undertaken to see if it is possible to attain the required specificity to chart slight changes in formulation from one batch of manufactured material (commercial grounds, tube paints) to the next.

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### Participating institutions

Van Gogh Museum, AMOLF, ETH Zürich, ICN

**CP:** Drs. E. Hendriks (Van Gogh Museum)

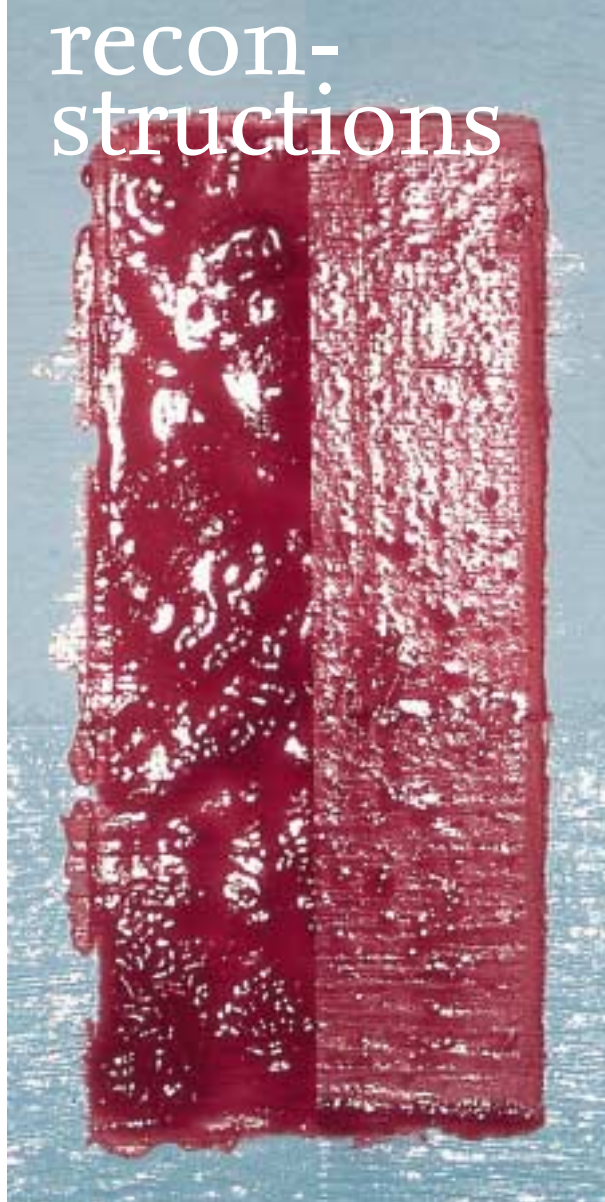
The Hart (Historically Accurate Reconstructions of Oil Paintings Composites) project provides reconstructions of paint and paint composites for specific projects under the De Mayerne Programme.

### Paint texture and paint defects

In the past, painters have exploited a wide range of textures, from the kind of highly impasted paint seen in Van Gogh's paintings and Rembrandt's highlights to the smooth, enamel-like surfaces found in the works of the Fijnschilders such as Dou or Van Mieris. How painters achieved such variety in texture is not fully understood. Although analysis can provide a list of most materials present, it is only by reconstructing oil paints using historically accurate materials and recipes that the proportions of the materials and their individual functions can be appreciated. Historically accurate reconstructions concentrating on lead white pigments, paint layer sequence and timing of paint application can help to unravel the mechanisms behind the development of these textures.

### Historical recipes

The Hart project centres on the use of historical recipes. These provide a rich source of information for



Rose madder oil paint used as a glaze, recreation using historical recipes - IMAGES Dr. L. Carlyle

modern researchers on the methods and materials used by artists in the past. By comparing a large collection of instructions for the preparation of pigments, drying oils, mediums, and varnishes over the centuries using two unique databases (ArTeS at ICN concentrating on Dutch art technological sources prior to 1800 and a database covering British sources dating from 1750-1900), it is possible to identify representative recipes and to track the introduction of new materials.

### Reconstructions

Recreating historical recipes not only results in a better understanding of the instructions, but often produces new and unexpected information in the process. Clear differences can be distinguished in the handling properties of lead white paint according to the degree of heat applied to the oil and the lead compound used.

### Historically accurate materials

When reconstructions are intended for use in molecular investigations of artists' varnishes, oils, mediums and pigments, it is imperative that they are made with historically accurate materials. Modern, commercially prepared drying oils available from artists' suppliers are not refined and processed in accordance with traditional methods. The lack of information on seed lots and pro-

cessing methods makes it impossible to compare the chemistry of one set of paint samples made with a commercial oil with another made at a different time using a different batch of oil. Mixing additives or mediums with modern tube paints in order to evaluate their effect on oil paint is equally problematic since modern tube paints no longer contain ingredients consistent with paints produced in the past. Linseed and poppy oils can be replaced by safflower oil, and pigments can be treated with modern chemicals to enhance their suitability in modern paint systems.

### Scientific examination of oil paintings

Reconstructions of old recipes are valuable not only for the new information gained during their preparation, but also because they provide scientists with representative samples essential to their work. Identifying individual components in samples from actual paintings can be problematic: some materials are difficult to find when they appear in a matrix of similar substances, and contemporary analytical standards for materials do not always reflect their chemical state after processing and prior to use in paint. Reconstructions using known materials will help establish the limits of detection for specific instrumentation and provide an invaluable reference set for further analytical work.



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### Participating institutions

ICN, Mauritshuis, Van Gogh Museum, Leiden University, AMOLF, Rijksmuseum

### CPI: Dr. L. Carlyle

(CCI – Canadian Conservation Institute, on secondment at ICN - Netherlands Institute for Cultural Heritage)

# Comparative studies of paintings

## COMPARATIVE STUDIES OF PAINTINGS IN THE ORANJEZAAL OF THE ROYAL PALACE HUIS TEN BOSCH

The Oranjezaal is the central hall of the Royal Palace Huis ten Bosch, home of the present queen. The painted decoration of the interior was commissioned by Amalia van Solms, wife of stadholder Frederik Hendrik. Between 1648 and 1652, twelve famous artists from the Northern and Southern Netherlands painted an allegorical scheme glorifying the life of the stadholder, who had died in 1647. This *trompe l'oeil* ensemble is now considered one of the most important works of the 17<sup>th</sup> century Netherlands. The commission for the execution of the interior went to twelve carefully selected painters who worked in various towns in both the Northern and the Southern Netherlands, including Haarlem, Amsterdam, The Hague, Den Bosch and Antwerp. Van Campen (the architect) instructed each of them on the desired composition, perspective, size and direction of light. Each painter was also provided with one or more canvases, which were prepared and primed by the same artisan. The colour of the priming was identical both for the canvases and for the painted decoration on wood. A consistent and moderate use of the room for receptions and festivities has kept the painted interior of the Oranjezaal in a fairly authentic condition. Furthermore, the paintings have been subjected to only a few restorations, datable from archival sources. The majority of the canvases have never been relined and are still fixed to the original stretchers.

The original paint layers on the architectural components of the room are still present.

The aim of the research is twofold. Firstly, it is to study the various pictorial and technical means used by these mid-17<sup>th</sup> century painters to create a pictorial illusion. Topics addressed by the comparative studies will include the rendering of modelling and illusion of space by colour, light and shade, and typical painterly tricks. The pigments and binding media used for various colours will also be compared and related to the different pictorial aims of the painters. Secondly, the condition of these pristine paintings will be compared with that of paintings which have been kept under less favourable environmental conditions. This will provide valuable insight into the extent to which painting techniques and environmental conditions influence the development of particular paint film defects. The research will involve the use of visual, photographic, microscopic, and micro spectroscopic and mass spectrometric imaging techniques. The interpretation of technique and style will also demand the study of contemporary texts on technical subjects and art theory.

The research conducted within the MOLART programme concentrated mainly on the chemistry of aged varnish,



Frederik Hendrik (detail),  
Gerard van Honthorst

Frederik Hendrik (detail),  
Gerard van Honthorst

Frederik Hendrik (detail),  
Thomas Willeboirts Bosschaert

Frederik Hendrik (detail),  
Jacob van Campen

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oil paint and egg tempera paint, the development of instruments for the analysis of paint in cross-section and the investigation of a number of paint film defects. In the De Mayerne programme we hope to use this knowledge for the interpretation of technical and stylistic phenomena in one of the most important works of art surviving from the 17<sup>th</sup> century Netherlands.

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## **Participating institutions**

SRAL, AMOLF, University of Groningen

## **CPI: Mrs. A. van Grevenstein**

(Director of SRAL – Limburg Conservation Institute)



Thomas Willeboirts Bosschaert, detail from Frederik Hendrik and Maurits as commanders, with in the distance the battle at Nieuwpoort, ca. 1650 - PHOTO SRAL

# De Mayerne

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### PARTICIPANTS IN THE FIRST STAGE

**AMOLF** (FOM Institute for Atomic and Molecular Physics), Amsterdam

**CCI** (Canadian Conservation Institute), Ottawa

**ICN** (Netherlands Institute for Cultural Heritage), Amsterdam

**Mauritshuis**, The Hague

**Rijksmuseum**, Amsterdam

**SRAL** (Limburg Conservation Institute), Maastricht

**UL** (Leiden University), Leiden

**Van Gogh Museum**, Amsterdam

### COLLABORATION WITH RESEARCHERS FROM INSTITUTIONS

Chicago Institute of Art, Chicago

Courtauld Institute of Art, London

ETH (Swiss Federal Institute of Technology), Zürich

Hamilton Kerr Institute, Cambridge

RKD (Netherlands Institute for Art History), The Hague

RUG (University of Groningen), Groningen

Tate Gallery, London

UvA (University of Amsterdam), Amsterdam

VU (Vrije Universiteit), Amsterdam

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