Scientific analysis of historical paint and the implications for art history and art conservation. The case studies of naples yellow and discoloured smalt.

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PRINCIPLES, METHODS AND PITFALLS

SCIENCE AND ART

The technical examination of works of art is mainly based on two paths of research, namely the examination of art technological sources and the scientific analysis of works of art. Art technological sources refer to historical records containing information on the production process of works of art. Examples range from manuscripts, in which an artist kept personal notes concerning the making of art, to original depictions of the artist's studio, showing tools, materials and organization of the production process of art. As is the case with all historical documents, the interpretation of such records is subject to the rules of historical criticism, as will be explained below. The second path in art technological research is based on the physical, chemical and sometimes biological analysis of the art object itself. Painting pigments, binding media and other painting materials can be subjected to scientific analyses, in which analytical methods from various scientific disciplines are applied. For the work to be discussed in this thesis X-ray powder diffraction was used as well as various other techniques.

Although a combination of two distinctly different disciplines can be attractive, many difficulties may arise during interdisciplinary collaboration. In essence they come down to the problem of interpreting research results from one discipline within the context of another. Crucial for effective collaboration is that scientists, conservators and art historians should be willing to understand something of one another's background and way of thinking. The scientist must become familiar with the art object and its historical context and problems; art historians and conservators must learn how scientific data are obtained and what sort of equipment is used. It is important to realize that each analytical technique has a set of strong points as well as limitations.

However straightforward and self-evident these conditions for interdisciplinary research may be, history has shown that such prerequisites have not always been fulfilled. In some cases, scientific methods of examination have been warmly welcomed by art historians or conservators and maybe even overestimated at first stage while being critized and/or forgotten later. A good example of such a development is the introduction of dendrochronology in the study of wooden art objects in the 1960's. In the art historical community this technique was first welcomed as an objective method for dating early European panel paintings. Once it was found out that certain wooden carriers may have been stored -sometimes for a substantial number of years- before being used as a panel, art historical interest in dendrochronology
decreased somewhat. As a conclusion, art historians, conservators and scientists should leave no doubts about the potentialities of certain analytical techniques. Overrated expectations can easily lead to miscommunication and will certainly result in less valuable research results.

The application of a new scientific technique in the examination of works of art sometimes makes the impression of exploring a new scientific 'gadget' without much thought about its potential, systematic use in art history. Therefore, when introducing a new scientific method to conservation science it is imperative to develop a methodology that takes into account the practical and repeating problems of art historians and conservators. Again, history has shown that this rather self-evident condition has not always been rigorously observed. The application of autoradiography, for example, in the examination of paintings has been introduced enthusiastically in the 1970's at the Metropolitan Museum of Art in NY. Since then, however, the technique has not been applied systematically in the study of works of art anywhere in the United States. A renewed, though somewhat adapted, use of this technique has proven to be more of a match to certain art historical questions, as recent projects at the Gemaeldegallerie in Berlin and the study in chapter 6 show. The advancement in analytical techniques throughout the sciences should be monitored constantly in order to assess their potentialities for conservation science. Close and regular collaboration seems to be a prerequisite for a fruitful application of scientific techniques in the study of art objects. Mutual understanding is the foundation for progress in this interdisciplinary work.

Studying the history of Naples Yellow and the discolouration of smalt required a research effort that involved both textual source investigation and scientific analysis of pigment material. Both paths of research, scholarly interpretation of source material as well as the scientific examination of art objects will be introduced below.

STUDY OF ART TECHNOLOGICAL SOURCES

The problem of dealing with historical documents is known in history as historical criticism. Historical criticism intends to bring the researcher closer to events that have taken place in the past. The historian should be conscious of the fact that every record of the past is a subjective report of history. Historical interpretation is carried out in order to distinguish appearance and reality, facts and opinions. The historical value of source documents can range from sincere and honest information to unconscious misrepresentation or even outright falsification. Along this line the historian needs to assess the historical value of each source individually.

At first sight, the interpretation of art technological sources seems to be a relatively simple and straightforward exercise. Sources like historical painting manuals or pigment production recipes seem to be a collection of fairly down-to-earth, matter-of-fact information. One would not expect the author of such practical textual sources to have any reason to knowingly mislead or deceive the reader. However, as will be shown below, even practical sources
concerning the production of art need to be evaluated critically before interpreting the information contained.

Art technological sources can be divided into two types. The first category concerns textual sources, such as painting manuals, alchemist books, treatises, contracts, manuscripts and other printed or written sources, in which art technological information is contained. The second category of sources includes pictorial representations of the artist's studio from which information on the production process of art can be deduced. In this thesis, however, only textual art technological sources have been used.

One of the first difficulties is to assess the scope of a source. A source must be dated and located and should be connected to the subject of study. The distribution and use of textual sources should be examined if possible. In any case, the question remains whether a certain textual source contains relevant contemporary information. Earlier studies have shown that the technical information in historical source literature is not always conform the current technological practice, but should rather be considered as a compilation of knowledge and methods used in the past. Reason for such anachronisms is the common practice of re-editing and compiling recipes and all sorts of technical information in so-called recipe books. This tradition started in the late Middle Ages and continued well into the 19th century. Only the introduction of the concept of intellectual property in modern times ended the copying of technical knowledge, including literature on the production of pigments. Therefore, there is never absolute certainty that the contents of technical production literature reflects contemporary historical practice.

Interestingly, various paintings pigments have been found on paintings that have been very scarcely referenced in historical literature. A good example is the yellow pigment lead-tin-yellow. This pigment was the most commonly used synthetic yellow pigment in northern European painting until the 1730's. After this date the pigment fell into oblivion only to be rediscovered in 1941. The currently known source literature, however, hardly mentions this widely used pigment. So far, no exact production recipes for this pigment have been found in technical production literature. Vice versa, the presence of some other pigments that do get mentioned often in the literature has hardly been established on historical paintings. For example, in many early Italian production recipes the manufacture of purporino, or Musivgold (SnS$_2$), is discussed in detail. Given the frequency of reference to this pigment one would expect an intensive use of this material on paintings. So far, however, this seemingly popular pigment has been found on a few paintings only.

Behind the practical, literal text of technological sources one may sometimes find deeper, abstract connotations. This was discovered during the study of 17th century Spanish painting techniques. In various painting manuals certain pigments were mentioned that could not be found on actual contemporary paintings by Velazquez and others. Most of the pigments that were mentioned in writing, but not used in practice, had already been described by Pliny the Elder in his famous Historia Naturalis. According to the researchers these pigments were
listed deliberately in contemporary painting manuals in order to accentuate the classical roots of the art of painting, thereby underlining its distinguished and venerable origin. In cases like these it is of importance to find out if and why a source deviates from historical practice.

In addition, it is important to find out for which audience a technical source was written. One has to be aware of the possibility that printed literature does not always frankly disclose trade and production secrets. Medieval guilds were well-organized trade associations that controlled the professional education. In general, protectionist guild regulations severely limited uncontrolled distribution of professional information, which was sometimes even threatened with capital punishment. An example of protectionism in art production will be encountered in this dissertation in the discussion of the 18\textsuperscript{th} century production history of Naples Yellow (see chapter 3).

Unpublished manuscripts on the other hand, intended for personal use of the artists, are more likely to reveal the trick of the trade. The problem with such personal documents is that these sources may be fragmentary. The author may have left out information that was too obvious or superfluous to himself, though necessary for the understanding of the reader nowadays. Recently, Van Eikema Hommes has shown that a comparative study of various European sources, often containing fragmentary information, gives a complementary and much more coherent insight into historical knowledge on painting technology.\textsuperscript{10}

Another problematic issue in the interpretation of sources is the use of complex historical terminology. In many cases the historical name for materials or pigments is unknown or differs from modern vocabulary. A well-known example is the difference between the Dutch words \textit{schelpwit} and \textit{lootwit}. Until recently it was unclear what was meant exactly by which terminology and whether there was any difference. Was \textit{schelpwit} (schelp being the Dutch word for shell or curl) a term for a lower quality of lead white, mixed with ground shells? Or was \textit{schelpwit} the name for a high-quality type of lead white which was kept in shells? Goedings et al. have shown convincingly that \textit{schelpwit} indicated a high-quality type of lead white as the term \textit{schelp} (or curl) should be understood as a reference to the shape in which basic lead carbonate was scraped of the curls of metallic lead during the production process.\textsuperscript{11}

Material research of art objects combined with comparative examination of textual sources can sometimes offer insight into such historical-terminological obscurities, as Wallert showed with the examination of a Greek vase and classical descriptions of pigments used in these days.\textsuperscript{12}

In conclusion, descriptions in art technological sources can deviate from actual practice in history for a variety of reasons. It is of importance to evaluate critically information contained in such sources. Comparison with results of scientific analysis can only take place after cautious interpretation.
CHAPTER I

SCIENTIFIC STUDY OF PIGMENTS

As mentioned above, various scientific disciplines are engaged in the analysis of paintings and painted objects. For the research discussed in this dissertation various analytical techniques were employed, which will be introduced individually in the appropriate chapters. The work discussed in chapters 2, 3 and 4 relies mainly, though not exclusively, on the analysis using X-ray diffraction, an analytical technique to investigate crystalline material. An introduction to the field of crystallography and its analytical techniques will therefore be given below.

Principles of Crystallography

As most pigments are of crystalline nature, crystallography is an important field in the scientific study of pigments. Crystallography is concerned with the description and the investigation of crystals. Originally the term crystal referred to a solid body bounded by natural plane faces, e.g. ice crystals. The description of the geometry of crystals, for which the foundation was laid in 1669 by the Danish scientist Nicolaus Steno, used to be the only occupation of the crystallographer. In the course of the 20th century, however, it became clear that the external termination of crystals by planar faces is only one aspect of a much more general behaviour of crystals. In modern crystallography the term crystal covers a much wider range of materials, including most pigments used in painting. Interestingly, crystals are not necessarily solid materials, as can be noticed in daily life when watching so-called liquid crystal display (LCD) computer screens. At the same time crystallinity is a gradual property of materials. Crystallinity can be low, as is the case in one-dimensionally periodic materials like strings of asbestos, or can be very high in highly symmetrical compounds like the painting pigment Naples Yellow.

Crystals can be described as a periodic repetition of a basic unit cell in which one or more symmetry-related sets of atoms are positioned. In other words, the exact repetition of identical groups of atoms at precisely equal intervals can be described using a three-dimensional grid system or translation lattice. It is important to note that the grid lines are drawn at equal

**Figure 1** Three-dimensional lattice showing a unit cell
intervals corresponding to the repetition distances within the crystal. As a consequence, the surroundings of each grid-line intersection, or lattice point, are identical. In such a three-dimensional lattice, the unit cell is a volume element and may be defined as the parallelepiped whose edges are successive grid lines (figure 1).

The three-dimensional stacking side by side of unit cells eventually produces the macroscopic crystal. A single crystallite, barely visible to the human eye, may consist of a repetition of millions and millions of unit cells. Obviously, the translation lattice is a mathematical construction that functions as a useful and necessary coordinate system to which the actual structure can be referred to. The three grid-line directions, or coordinate axes are denoted as X, Y, and Z. The lengths of the unit cell edges along these axes are termed a, b and c, respectively. The angles between the axes are called α (between b and c), β (between a and c), and γ (between a and b, resp.). Figure 2 shows the most basic division into 7 crystal systems.

Three points of a translation lattice define a so-called lattice plane. All members of a set of parallel lattice planes are occupied in an identical fashion by lattice points. The distance d between each two successive lattice planes is constant. The orientation of the lattice planes in the lattice is characterized by means of the so-called Miller indices, three integers usually termed h, k, and l, that define the points of interception along the a (a/h), b (b/k), and c (c/l) axis of the member of the set of parallel lattice planes closest to a chosen origin in the translation lattice. Miller indices are used for various purposes, amongst others to designate a set of lattice planes, a particular member of the set or the face of a macroscopic crystal parallel to the set. As will be discussed below, Miller indices are also of major importance for X-ray diffraction study of crystals, the most fundamental analytical instrument in modern crystallography.

In addition to the periodic repetition of the unit cell a second factor contributes to the geometric regularity of crystals: the existence of symmetry in the unit cell and the crystal. Macroscopic symmetry operations in crystallography are based on two simple types of symmetry: rotation axes and rotation-inversion axes. Both elements may be combined to produce a more complex symmetry. Based on these crystallographic principles crystals can be divided in 7 crystal systems.
systems and subdivided into 32 point groups. At the atomic level more types and combinations of symmetry operations (screw axes, glide planes) are possible that lead to three-dimensional periodic stacking, resulting in a total of 230 so-called space groups.

X-rays

As mentioned above, X-rays are of crucial importance in the study of crystals. X-rays have been discovered by Wilhelm Röntgen in 1895, but at that time the nature of this type of radiation was not clear yet. In fact, it was not until diffraction by crystals was observed experimentally that the wave character of X-rays was proved. X-rays are the part of the electromagnetic radiation that lies between the ultraviolet spectrum and gamma rays, with a wavelength ($\lambda$) ranging from 0.1 Å to 100 Å (figure 3).

The usual way to produce X-rays consists of accelerating electrons using high voltage and subsequently slowing them down rapidly by directing them against a metal target. In this process the electrons energy of motion is converted into quanta of radiation. The distribution of intensity of the radiation emitted depends on the accelerating voltage, as well as on the type of target material. In addition to a broad maximum of radiation (so-called white radiation) a number of nearly monochromatic, high intensity peaks occur (Fig. 4). These peaks are the characteristic lines for the elements of which the target is made. As will be explained below, for the diffraction techniques employed in this study the X-rays used should be as monochromatic as possible. Thus, a single peak of radiation is selected for experimental work, while the white radiation and other peaks are filtered out.
X-ray diffraction

The diffraction of X-rays by crystals was discovered in 1912 by the German scientist Max von Laue. In the same year William Bragg noted the similarity of diffraction of crystals to ordinary reflection. Bragg deduced a simple equation treating diffraction as 'reflection' from planes in the translation lattice of a crystal. A beam of X-rays falling on a crystal will be scattered. This effect can be considered as reflection by all lattice planes simultaneously. Constructive interference occurs only when all the scattered waves are in phase, i.e. when the path difference is an integral multiple (n) of the wavelength λ, as exemplified in figure 5. This gives the condition that the incident and reflected beam must have the same angle θ with respect to the crystal plane and can be expressed in the formula which came to be known as Bragg's Law:

\[ 2d \sin \theta = n\lambda \]

When exposing a crystal to a beam of monochromatic X-ray radiation, diffraction can be observed at a limited amount of angles corresponding with the specific d-spacings of the crystal and depending on the unit cell parameters. The relative intensities of these reflections depend on the arrangement of atoms within this cell. Therefore, the diffraction pattern consisting of diffraction angles and corresponding relative intensities of the reflections is characteristic of the crystal structure. Based on these principles, different types of X-ray diffraction can be performed on crystalline materials, amongst others single-crystal diffraction and polycrystalline (or powder) diffraction.

Single-crystal diffraction

Examination of sufficiently large individual crystals by diffraction of X-rays or electrons is known as single-crystal diffraction. In order to record diffracted beams from a single-crystal when using monochromatic radiation the orientation of the crystal with respect to the incident radiation has to be varied. The diffracted beams appear as a three-dimensional pattern of spots, with varying intensity and distances to each other. This pattern can be recorded on sensitive photographic film or with a (two-dimensional) digital detector. In this thesis single-
crystal diffraction was hardly used, except for one case using single-crystal electron
diffraction in a transmission electron microscope (chapter 4). Crystalline painting pigments
are usually randomly distributed in the binding media and the size of powdered pigment
crystallites, ground before being mixed with binding media, is usually too small to enable
single-crystal X-ray diffraction. Therefore, polycrystalline or powder diffraction is a much
more suitable technique to study painting pigments.

X-ray powder diffraction

Ideally, powdered crystalline material consists of an assembly of a large amount of randomly
oriented crystallites. If a powder sample is exposed to a beam of X-rays, the beam runs
through the powder sample, and meets a very large number of crystallites, each crystallite
having a different orientation. A substantial number of these crystallites, however, has an orientation that fulfills
Bragg's law as described above. Whenever a crystallite has a particular set
of hkl planes that makes the appropriate glancing angle $\theta$ a diffraction signal
occurs, making an angle of $2\theta$ with the incident beam of X-rays. Fig. 6 shows a
geometry of X-ray powder diffraction (XRPD).

The locus of directions making an angle $2\theta$ with a given direction is a cone of half-
opening angle $2\theta$. For each solution of the Bragg equation such a cone exists:

$$\theta = \sin^{-1} \left( \frac{\lambda n}{2 d_{hkl}} \right)$$

When a sufficiently numerous amount of crystallites fulfills this condition, the cone-shaped
diffraction signal produces a number of concentric rings at the detection end. Usually, the
sample is rotated around one or more axes so that each crystallite adopts various orientations,
thereby increasing the chance of contribution to the diffraction signal. From a measurement of
the radius of the circle, the known sample-to-detector distance and the given wavelength of
the X-rays one can easily calculate the cone angle and thereby determine $\theta$. As has been
shown above, the angles $\theta$ at which a crystal may reflect X-rays depend fundamentally on the interplanar spacings $d_{hkl}$ that themselves depend on the dimensional characteristics of the crystal's unit cell. The relative intensities of the various reflections depend on the arrangement of atoms within the unit cell. The combination of unit cell and the atom positions in it comprise the crystal structure itself. A powder diffractogram or diffraction pattern, consisting of a set of reflections at various $\theta$ angles with certain relative intensities, may therefore be used as a fingerprint to characterize the crystalline material.

The most widely used application of X-ray powder diffraction (XRPD) is for identification of crystalline material. Over the past 70 years a database of diffraction patterns has been developed, containing well over 100,000 crystalline phases. This database is known as the Powder Diffraction File (PDF) and is updated by the Joint Committee for Powder Diffraction Standards (JCPDS). When compared to this database, a diffractogram can be used to identify the crystalline phase.

Based on the theory discussed above a number of different X-ray powder diffraction devices can be constructed, either using a sensitive photographic film or a digital X-ray detector to record a diffractogram. Below, those techniques that were employed in the present study will be discussed shortly.

1. Debye-Scherrer camera

One of the oldest but still very popular methods of XRPD is performed using the so-called Debye-Scherrer camera, a simple powder diffraction camera technique, which is widely used in conservation science labs around the world. Fig. 7 outlines the camera. In this type of camera, the recording film is a photographic strip, which is placed on a cylindrical drum centred around the sample. The main body of the camera holds a collimator that defines the incident beam of X-rays. At the opposite side a beam trap stops the incident beam. The powdered sample material is usually put into a glass capillary, which is then placed in the beam of X-rays. In the case of samples taken
from paintings, a tiny flake of paint is put on top of a glass spindle using vaseline as adhesive material. Since the diffraction signal travels through the sample holder, this setup is called transmission mode.

An important drawback of the Debye-Scherrer method, however, is the fact that the diffraction lines are fairly broad. Separating several lines close to or on top of each other can be a difficult exercise. If multiple phases are present within one and the same sample, it is crucial to have a clear set of sharply defined reflections. Decreasing the aperture in the collimator, thus narrowing the beam of X-rays, is the only, rather limited method to obtain a higher resolution, i.e. more resolved diffraction lines on the film.

2. Guinier camera

For the purpose of high-resolution data acquisition, André Guinier developed another diffraction technique.\textsuperscript{14} The Guinier camera is an example of a focussing X-ray diffraction technique. In this case the sample is placed along an arc of a circle, which is irradiated by transmission. The arc subtends equal angles at every point on the circle. The diffracted radiation will converge in both cases on the focussing circle of the camera, thus producing a very sharp line on the film. The focussing beam is usually produced by a bent crystal monochromator, leading to a much sharper diffraction signal on the film. The main disadvantage is that this technique only covers a limited $2\theta$ range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{guinier_camera.png}
\caption{geometry of a Guinier camera}
\end{figure}
3. Diffractometers

Both the Guinier and Debye-Scherrer cameras use films to record the intensity and position of diffracted X-rays. Instead of a film a digital quantum counter detector can be used. Instruments using such a digital detector to record the intensity and position (= Bragg angle) of the diffraction pattern are called powder diffractometers. Examples of such diffractometers, used extensively in the present thesis, are the Philips X'Pert Pro and the X'Pert I. The X'Pert Pro system makes use of a special monochromator, which only puts through the CuKα₁ component of copper radiation, resulting in a highly monochromatic incident beam of radiation. In addition, diffraction experiments can be run in transmission or reflection mode. Also, the incident X-rays can be set to a parallel beam or a focused beam. The setup of the X'Pert allows for the analysis of small objects, which will be used in chapter 2. In this way, sample-free XRPD analysis becomes possible without causing harm to the object under study.

4. Synchrotron radiation diffraction

Various forms of electromagnetic radiation, including X-rays, are generated in so-called synchrotron radiation facilities, such as the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The ESRF is the world’s first 3rd generation synchrotron facility, operating a storage ring of 6 GeV.

Particles traveling through an accelerating field are known to emit electromagnetic radiation. When charged particles are moving at a speed approaching that of light, a spectrum of radiation is emitted that extends into the hard X-ray region. This radiation is emitted in a very narrow cone parallel to the instantaneous velocity. At the ESRF electrons are accelerated in a closed circuit so that the radiation is generated in cones tangent to the path followed by the electrons. At every bending magnet of the accelerator ring electrons are accelerated and consequently radiation is generated.

X-rays produced here are in many ways superior, offering a brilliance (expressed as $\text{photons}^{-1}\text{s}^{-1}\text{mm}^{-2}\text{mrad}^{-2}$ at 0.1% Bandwidth $\Delta\lambda/\lambda$) that is about $10^{18}$ higher than that of a standard X-ray tube. This radiation can be used for various experimental techniques, including high-resolution X-ray powder diffraction, which was performed on a number of Naples Yellow samples in the present study (see chapter 4).
CHAPTER 1

NOTES


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